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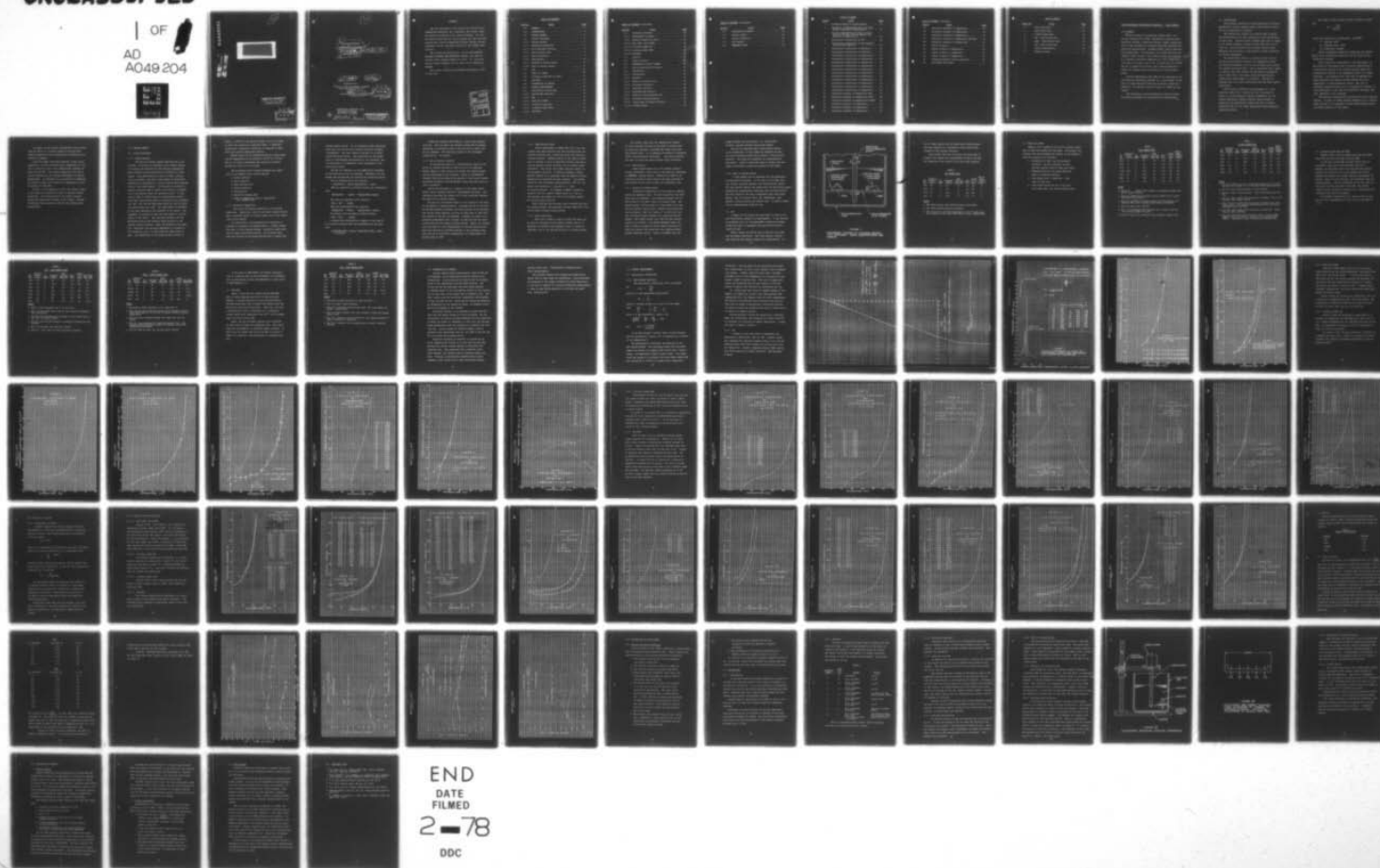
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HIGH PERFORMANCE PYROELECTRIC MATERIALS. (U)  
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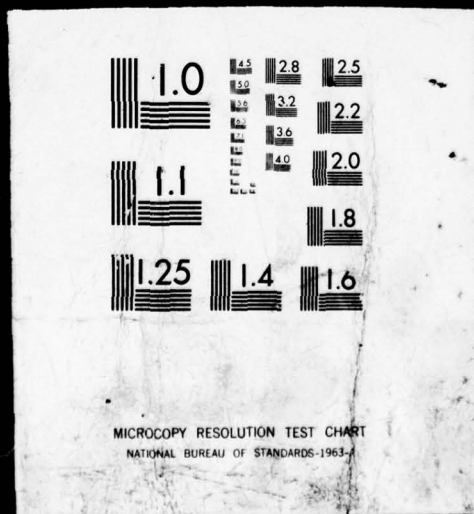
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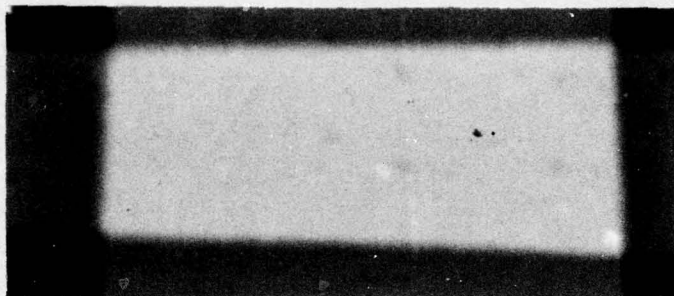




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6 HIGH PERFORMANCE  
PYROELECTRIC MATERIALS.

9 Final Report. Feb 75 - Jun 77,  
by  
Warren/Ruderman

10

11 Jun 77

12 86p.

Prepared for:

NIGHT VISION LABORATORY, USAECOM  
Fort Belvoir, Virginia

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Contract DAAK02-75-C-0131 new

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## FOREWORD

The work described in this report was carried out by INTERACTIVE RADIATION, INC., Northvale, New Jersey, under the technical direction of Dr. Warren Ruderman. Mr. Eric Martindale supervised the crystal growth, Mr. Hans Nothnick prepared the crystals samples and targets, and Mr. Richard Ujazdowski and Mr. John Zola carried out the crystal measurements.

The program was initiated by the US ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT CENTER, Fort Belvoir, Virginia under Contract DAAK02-75-C-0131. Dr. Lynn Garn was the Project Engineer for the Night Vision Laboratory, USAECOM.

This report covers work performed from February 1975 to June 1977.

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## 1.0 SUMMARY

Single crystals of triglycine sulfate (TGS), triglycine fluoberyllate (TGFB), deuterated triglycine fluoberyllate (D-TGFB), triglycine selenate (TGSe), mixed crystals of TGS and TGSe and l-alanine doped TGS and TGFB were grown and characterized. Optimum crystal growth conditions were established. In particular, for D-TGFB which has the highest figure of merit, best crystal growth was obtained at a starting saturation temperature of 45°, a seed rotation rate of 15 rpm, a pH of 3.6, a growth rate of 0.1° per day for a volume of 10 liters, and a seed orientation in which the cleavage plane was parallel to the horizontal plane. *degrees*

Careful measurements were made of the pyroelectric coefficient and dielectric constant of a large number of samples of these homologs of TGS and consistent values were obtained. The superior figure of merit of D-TGFB was confirmed.

The production of thin pyroelectric crystal targets by optical polishing and cup-etching was investigated. *↑*



## 2.0 INTRODUCTION

The principal objective of this program was to develop pyroelectric crystal targets having a high figure of merit for use in pyroelectric vidicons.

The pyroelectric vidicon is a vidicon tube in which the photoconductor has been replaced by a thin pyroelectric crystal plate. Radiation from a thermal body that is imaged on the target produces a dynamic charge image that can be read out. Garn and Sharp<sup>1</sup> have reviewed vidicon target materials and the effect of pyroelectric crystal properties on vidicon performance.

The pyroelectric effect in crystals arises from the electrical polarization induced by a temperature change. All crystals belonging to one of the ten polar point groups can exhibit pyroelectricity. Only a relatively small number of crystals have been studied for pyroelectric properties and of these only a very small group have pyroelectric coefficients large enough to be useful. TGS and its homologs have very large coefficients and have been studied extensively.

Three factors affecting the performance of a pyroelectric crystal for a vidicon are: (a) the figure of merit,  $M$ , in the absence of lateral conduction, (b) the thermal modulation transfer function which provides a measure of the pyroelectric signal lost due to thermal conduction and (c) the target capacitance which determines image persistence.

The figure of merit which we shall consider is given by:

$$M = \frac{P(T)}{c_p \cdot d \cdot \epsilon_r}$$

where  $P(T)$  = pyroelectric coefficient, coul/cm<sup>2</sup>°C

$d$  = density, g/cm<sup>3</sup>

$c_p$  = specific heat, J/g°C

$\epsilon_r$  = dielectric constant

Recent studies<sup>2</sup> have shown that D-TGFB has the highest value of  $M$ , principally because of the low value of the dielectric constant.

Lock<sup>3</sup> reported an improvement in the performance of TGS resulting from doping with l-alanine. Substitution of l-alanine for glycine in the crystal lattice causes the ferroelectric domains to be permanently poled in a single direction. The internal bias field that is produced prevents depoling from thermal cycling through the Curie temperature or from mechanical stress. The risk of accidental depoling during use of a pyroelectric crystal is thus eliminated. In the case of pyroelectric vidicons, however, depoling is not a problem.

The degree of internal bias increases with the l-alanine content. In order to obtain uniform response of an l-alanine doped crystal it is necessary to have uniform doping across the useful aperture of the target.



An object of the present investigation was to determine the effect of l-alanine doping of TGS and TGFB crystal properties such as pyroelectric coefficient and dielectric constant.

Keve<sup>4</sup> has shown that mixed crystals of TGS (Curie temperature of  $49^{\circ}$ ) and TGSe (Curie temperature of  $22^{\circ}$ ) can be tailored to have Curie temperatures anywhere between  $22^{\circ}$  and  $49^{\circ}$ . The crystal composition can therefore be adjusted to give optimum performance at ambient temperatures. An objective of our work was to determine the figure of merit as a function of temperature of mixed crystals of TGS-TGSe.

Finally, it is desirable to thin the crystal target to the range of 15 microns in order to improve vidicon resolution. The limiting factor for single crystals becomes the mechanical strength of the target. Methods of producing thin targets of TGS and its homologs were investigated.

### 3.0 CRYSTAL GROWTH

#### 3.1 Growth Techniques

##### 3.1.1 General Method

The basis of crystal growth from solution is as follows: A solution is prepared of the crystal species to be grown and saturated at some desired temperature. Seed crystals of high perfection are mounted on a seed holder. Such seeds should be free of cracks, strains, veils, inclusion and have a high degree of crystalline perfection as exhibited by a narrow rocking curve obtained with an x-ray spectrometer. The solution is placed in a vessel, generally made of glass, and raised to a temperature a few degrees above the saturation point. In the case of TGFB or D-TGFB lucite or polycarbonate plastic tanks were used because glass is attacked by the fluoberyllic acid. For TGS and TGSe glass tanks and lucite shafts and seed holders were used. The seed holder is preheated to the same temperature and inserted in the vessel. The equipment is arranged so that the seed holder is rotated slowly in the vessel. This provides agitation for the saturated solution and presents fresh solution to the growing crystal surfaces. After the surface of the seeds have dissolved, the solution temperature is lowered to the saturation point, at which time the seeds start to grow. The temperature of the solution must be held to



within  $\pm 0.005^{\circ}\text{C}$  of the desired temperature at all times to avoid the initiation of spurious seeds. A precision proportional temperature controller is required to maintain such precise temperature control.

Crystal growth can be effected either by slowly lowering the temperature of the solution ( $0.05^{\circ}$  to  $0.2^{\circ}$  per day) or by slowly evaporating the solution by passing through dry clean air or nitrogen.

The following crystal growth parameters are important in the growth of any crystal species:

1. Purity solution
2. pH of solution
3. Seed rotation rate
4. Seed orientation
5. Seed quality
6. Method of holding seed
7. Rate of temperature drop or evaporation rate (growth rate)

### 3.1.2 Materials Preparation

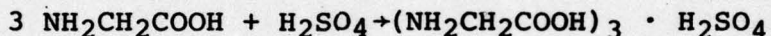
The purity of starting materials is of critical importance. Impurities, even in very small concentrations, have a profound effect on crystal growth and on the properties of the crystal.

All water used in the preparation of solutions or cleaning of equipment is obtained from a Millipore system. Tap water is first passed through a prefilter under pressure to remove particulate matter. The filtered water then goes through an activated charcoal bed to remove dis-

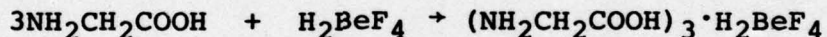
solved organic matter. An ion exchange column containing both anion and cation resin removes dissolved inorganic contaminants. The final stage is through a 0.6 micron teflon Millipore filter. The resistivity of the output water is continuously monitored by an in-line meter, and is maintained at 18 megohm-cm, which represents a very high quality water.

TGS and its homologs are not commercially available in the high purity that is required. Therefore, all compounds were synthesized and purified by recrystallization.

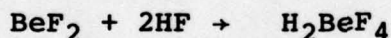
TGS was synthesized by the reaction:



TGFB was prepared by reacting glycine and fluoberyllic acid:



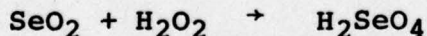
The acid was prepared by the reaction:



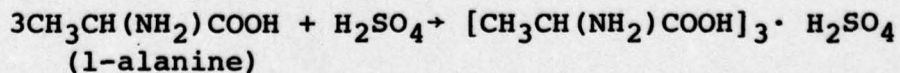
TGSe was synthesized by the reaction:



The selenic acid was made by oxidizing  $\text{SeO}_2$ :



L-alanine was introduced as a dopant in the form of tri-l-alanine sulfate which was synthesized by the reaction:





D-TGFB was prepared from TGFB by a three step exchange with  $D_2O$ . Only the amino and carboxyl groups and the  $H_2BeF_2$  exchanged; the hydrogen atoms on the  $CH_2$  are not labile and do not exchange. The deuterium content of the exchanged groups was 95 - 97 percent.

### 3.1.3 pH of Nutrient Solution

At equivalence there is a characteristic value of the pH for an aqueous solution of TGS or one of its homologs. Either higher or lower values will affect the crystal growth and the morphology of the crystals. There is considerable evidence that the pH affects the quality of the crystal growth and favors different crystallographic forms when more than one form is possible.

The pH was measured on a sample of a few cubic centimeters using a Beckman Model SS-2 Expandomatic pH meter. The reference electrode was calomel and a glass electrode (Ag/AgCl) was used for the unknown sample.

The pH has a pronounced effect on the solubility and hence on the degree of supersaturation. Although high pH in the case of the KDP homologs increases the cross section of the crystals and low pH causes tapering, we have not been able to find similar effects in TGS and its homologs. Instead, we found in exploratory experiments that a higher or lower pH from the equivalence point did not improve crystal growth. Hence, all crystal runs were made at a pH corresponding to the equivalence point. This was achieved by recrystallization in the synthesis step. Since the pH is affected by temperature, all measurements of pH were made at  $25^{\circ}C$ .

#### 3.1.4 Seed Rotation Rate

Recent experiments at INRAD have led to the conclusion that seed rotation rate and stirring within the nutrient solution play a much more vital role than previously believed. Adequate motion of the seed is necessary to prevent a layer of depleted solution from starving the growing crystal surfaces, and to prevent supersaturation. The latter can produce spurious seeds, as can excessive stirring. In order to produce a highly perfect crystal it is necessary that the degree of supersaturation be optimized and kept constant. The growth should be free from sharp discontinuities. That is, the growth rate should be a constant or a slowly varying function. For example a sudden increase in rotation rate will almost always result in a veil or flaw because the growth rate will be increased rapidly by the more rapid stirring.

These findings have now been used to modify the crystal growth process, and equipment has been modified to optimize highly uniform crystal growth.

#### 3.1.5 Seed Orientation

There are a number of ways in which the seeds can be held and oriented in the crystal rotator, and it is important to optimize this parameter since it plays an important role in the quality and rate of crystal growth.



The crystal faces that are exposed more readily to fresh nutrient solution as the seed is rotated tend to grow more perfectly, provided that these faces have high growth rates. It is generally desirable to determine which crystallographic directions grow most perfectly and then to orient the seed to favor those directions.

#### 3.1.6 Seed Quality

Seeds should always be of the highest possible crystal perfection, since flaws in the seed are replicated in subsequent crystal growth. Selection of seeds is an iterative process in which some of the best sections of each growth run are used as seeds for subsequent runs.

#### 3.1.7 Methods of Holding Seeds

It has been conventional to hold seeds by clamping gently two opposite sides. We have found that this technique has two drawbacks. The clamping pressure can induce strain in the seed which can produce flaws. The flawed crystal section grows at a much higher rate than the more perfect crystal part, thereby intensifying the strain problem. When this begins it is often the case that the whole crystal becomes very large and heavily flawed. The flawed crystal also robs the more perfect crystals of nutrient. The second drawback comes into play if there is growth in two or three directions because the crystal then grows over the clamping holder, thereby producing strain. There is evidence that the

clamp disturbs the flow pattern of the nutrient solution, thereby inducing non-uniform growth.

TGS and its homologs tend to grow almost equally in all directions, so that seeds are cemented and held on a flat horizontal plate which rotates in the nutrient solution. The seeds are therefore not constrained by the holder. Figure 1 shows that type of holder used and seeds of different orientation mounted on the holder.

### 3.1.8 Rate of Crystal Growth

A slow growth rate is desirable for the production of high quality crystals. If the rate is too high, veiling, strain, spurious seeding, and occlusions may result. For each crystal species the growth rate was determined experimentally and was maximized consistent with the high quality that was required. The rate is dependent upon other parameters, such as rotation rates, pH, temperature, seed quality, solution purity and crystal size. A typical growth rate is approximately 0.6mm per day.

### 3.2 TGS

A number of TGS growth runs were made in order to obtain high quality samples for measurements. It was desired to establish that all the measurement techniques yielded values that were in agreement with previously reported values for TGS.

Table 1 shows the growth runs of TGS that were made and the growth conditions. Very high quality crystals were obtained and samples prepared for measurements. In



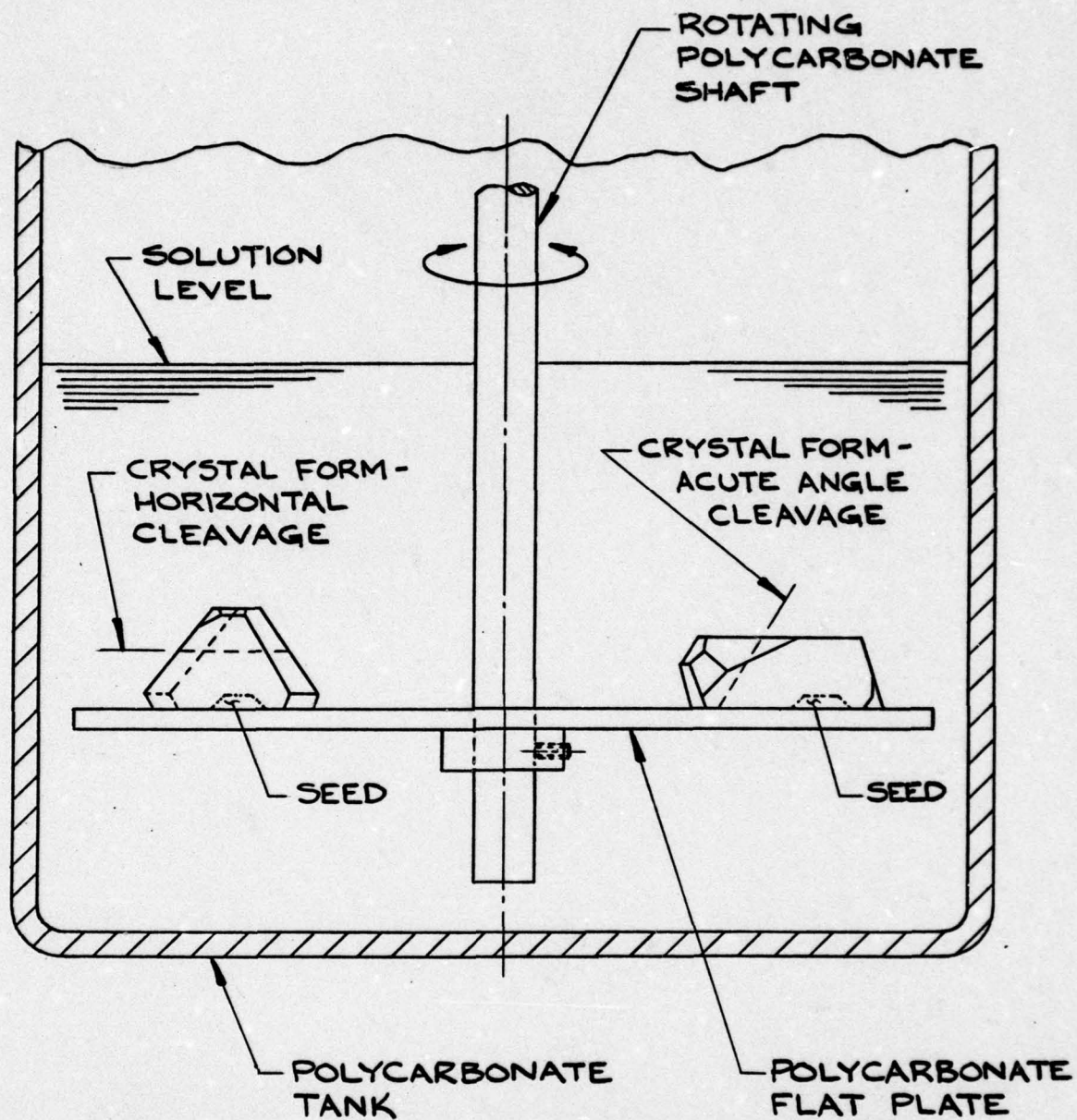


FIGURE 1

PREFERRED METHOD OF HOLDING SEEDS.  
TWO DIFFERENT SEED ORIENTATIONS ARE  
SHOWN.

all of these growth runs the seeds were cleaved plates and were cemented to a horizontal lucite plate which rotated in the nutrient solution.

The crystal from runs 16-15 and 11-8 were used to prepare test samples for measurements of TGS to be used for comparison with results of all the other homologs.

TABLE 1  
TGS GROWTH RUNS

| Run No. | Volume of Solution liters | No. Seeds | Saturation Temp <sup>o</sup> C | Seed Rotation Rate, RPM | pH at 21 <sup>o</sup> C | Length of run days | Seed to Shaft Distance, Inches |
|---------|---------------------------|-----------|--------------------------------|-------------------------|-------------------------|--------------------|--------------------------------|
| 16-4    | 25                        | 4         | 45                             | 15                      | 2.2                     | 35                 | 4                              |
| 16-5    | 22                        | 5         | 45                             | 6                       | 2.1                     | 118                | 4                              |
| 11-6    | 14                        | 4         | 42.5                           | 15                      | 2.8                     | 109                | 4                              |
| 11-8    | 21                        | 5         | 67.2                           | 6                       | 2.2                     | 77                 | 4                              |

NOTES:

1. The seed rotation was reversed every two minutes.
2. All runs yielded excellent crystals.
3. Run 11-8 with a starting temperature of 67.2<sup>o</sup> gave similar results to the other runs made at lower temperatures.



### 3.3 TGFB and D-TGFB

Tables 2 and 3 summarize the various crystal growth runs of TGFB and D-TGFB that were made. The general conclusions that were reached with respect to the growth of these two species is as follows:

1. Perfection of seed was the paramount parameter and was essential to good quality crystals free of flaws and cracks.
2. Mechanical work on the seeds should be kept to a absolute minimum.
3. Slow growth rate is important - less than  $0.1^{\circ}$  per day.
4. Seed holder should not be of the pressure clamp type, but rather, cemented down.

TABLE 2

TGFB GROWTH RUNS

| <u>Run No.</u> | <u>Volume of Solution liters</u> | <u>No. Seeds</u> | <u>Saturation Temp<sup>°C</sup></u> | <u>Seed Rotation Rate, RPM</u> | <u>pH at 21°C</u> | <u>Length of run days</u> | <u>Seed to Shaft Distance, Inches</u> |
|----------------|----------------------------------|------------------|-------------------------------------|--------------------------------|-------------------|---------------------------|---------------------------------------|
| 20-2           | 9                                | 4                | 44                                  | 15                             | 3.6               | 60                        | 3.5                                   |
| 20-3           | 9                                | 4                | 41                                  | 15                             | 3.6               | 135                       | 3.5                                   |
| 11-9           | 9                                | 4                | 41.7                                | 15                             | 3.6               | 40                        | 3.5                                   |
| 11-10          | 10.5                             | 8                | 42.1                                | 15                             | 3.6               | 96                        | 3.5                                   |
| 20-4           | 12                               | 4                | 46.6                                | 20                             | 3.6               | 22                        | 3.5                                   |
| 20-5           | 12                               | 4                | 45.6                                | 20                             | 3.6               | 81                        | 3.5                                   |
| 11-11          | 9                                | 4                | 43.6                                | 15                             | 3.6               | 127                       | 3.5                                   |

NOTES

1. Run 11-9 ended early because of excessive growth rate which caused flawing.
2. Run 20-4 ended early because of poor growth due to acute angle seed orientation.
3. Run 20-3 produced two good crystals with horizontal orientation and 2 poor crystals with acute orientation.
4. Run 20-2 gave fair crystals.
5. Run 11-10 produced good crystals but of small size due to the large number of seeds.
6. Run 20-5 and 11-11 produced large crystals (approx 5cm).



TABLE 3

D-TGFB GROWTH RUNS

| <u>Run No.</u> | <u>Volume of Solution liters</u> | <u>No. Seeds</u> | <u>Saturation Temp<sup>°C</sup></u> | <u>Seed Rotation Rate, RPM</u> | <u>pH at 21<sup>°C</sup></u> | <u>Length of run days</u> | <u>Seed of Shaft Distance, Inches</u> |
|----------------|----------------------------------|------------------|-------------------------------------|--------------------------------|------------------------------|---------------------------|---------------------------------------|
| 22-1           | 8.5                              | 4                | 44                                  | 15                             | 3.9                          | 95                        | 3.5                                   |
| 22-2           | 8                                | 8                | 42.5                                | 15                             | 3.9                          | 78                        | 3.5                                   |
| 22-3           | 8                                | 4                | 46.4                                | 15                             | 3.9                          | 71                        | 3.5                                   |
| 22-4           | 7.5                              | 4                | 45                                  | 15                             | 3.95                         | 96                        | 3.5                                   |
| 22-5           | 7.0                              | 4                | 43                                  | 15                             | 3.9                          | 21                        | 3.5                                   |
| 22-6           | 7.0                              | 4                | 39.4                                | 15                             | 3.9                          | 69                        | 3.5                                   |

NOTES:

1. All the D-TGFB runs had a deuterium content of 92.4 atom percent with respect to all the labile hydrogen positions.
2. Run 22-5 was aborted because of poor growth.
3. Run 22-1 gave 3 good crystals. Seed orientation was random.
4. Run 22-2 had 8 seeds with horizontal cleavage. Six of the crystals were badly cracked.
5. Run 22-3 had 3 seeds with horizontal cleavage and 1 with acute angle. All crystals had some cracks but horizontal cleavage seeds were best.
6. Run 22-4 had 4 seeds with horizontal orientation. Three crystals were flawless.
7. Run 22-6 had seeds held vertically with a lucite paddle added to assist stirring. Three of four crystals had cracks. Conclusion: vertical mounting unsatisfactory.

### 3.4 1-Alanine Doped TGS and TGFB

Tables 4 and 5 list the growth runs that were made. Seven TGS runs and five TGFB runs were made.

In the case of TGS-TLAS, initial efforts were unsuccessful, even with a high TGS:TLAS ratio of 4. However, we discovered that if we used the best quality crystal from the first run in the second run, and repeated this process, the crystal quality continuously improved. Thus, run 13-6 was poor, but successive runs improved steadily. This is attributed to the fact that in the first run with pure TGS as the seed, the initial crystal layers containing 1-alanine see a significant discontinuity and strain is induced.

The highest concentration of 1-alanine that we were able to grow corresponded to a mole ratio of TGS:TLAS of 1:1.5.



TABLE 4

TGS - TLAS GROWTH RUNS

| Run No. | Volume of Solution liters | No. Seeds | Saturation Temp °C | Seed Rotation Rate, RPM | pH at 21°C | Length of run days | Mole Ratio TGS : TLAS |
|---------|---------------------------|-----------|--------------------|-------------------------|------------|--------------------|-----------------------|
| 13-6    | 2.5                       | 3         | 39                 | 4.5                     | 2.3        | 121                | 4:1                   |
| 13-7    | 2.5                       | 2         | 37.6               | 4.5                     | 2.3        | 140                | 4:1                   |
| 13-8    | 2.5                       | 3         | 69                 | 4.5                     | 2.3        | 7                  | 4:1                   |
| 13-9    | 2.5                       | 3         | 63                 | 15                      | 2.5        | 68                 | 4:1                   |
| 25-8    | 2.8                       | 3         | 37.5               | 4.5                     | 2.5        | 27                 | 4:1                   |
| 25-9    | 3.0                       | 4         | 68                 | 4.5                     | 2.0        | 100                | 1:1                   |
| 31-2    | 3.0                       | 3         | 47                 | 4.5                     | 2.3        | 13                 | 1:1.5                 |

NOTES:

1. Seed to shaft distance was 2" in all runs.
2. Run 13-8 was ended early because the solution developed a dark coloration.
3. Run 25-8 was unloaded early because of poor growth due to the high l-alanine content.
4. Run 31-2 was aborted because of excessive cracking of the crystals.
5. Run 13-6 produced one excellent crystal.
6. Runs 13-7, 25-9, and 13-9 gave excellent crystals.

TABLE 5

TGFB - TLAFB GROWTH RUNS

| <u>Run No.</u> | <u>Volume of Solution liters</u> | <u>No. Seeds</u> | <u>Saturation Temp °C</u> | <u>Seed Rotation Rate, RPM</u> | <u>pH at 21°C</u> | <u>Length of run days</u> | <u>Mole Ratio TGFB:TLAFB</u> |
|----------------|----------------------------------|------------------|---------------------------|--------------------------------|-------------------|---------------------------|------------------------------|
| 31-1           | 2.0                              | 3                | 76                        | 15                             | 3.6               | 57                        | 1:2                          |
| 26-12A         | 2.0                              | 5                | 40                        | --                             | 3.6               | 0                         | 1:1.5                        |
| 26-12B         | 2.0                              | 5                | 46                        | 15                             | 3.6               | 18                        | 1:1.5                        |
| 26-13          | 2.8                              | 3                | 42                        | 4.5                            | 3.6               | 5                         | 1:0.67                       |
| 23-9           | 2.8                              | 3                | 44                        | 15                             | 3.6               | 120                       | 1:1                          |

NOTES:

1. The seed to shaft distance in all cases was 2".
2. Runs 26-12A and 26-12B grew poorly with excessive strain and cracks because of the high l-alanine content and were ended early.
3. Run 26-13 was unloaded because the seeds fell off the holder.
4. Run 31-1 was continued for seed development only. The original seeds dissolved because of improper saturation temperature assessment.
5. Run 23-9 was the best run and gave good crystals.



In the case of TGFB-TLAFB, the highest concentration of l-alanine that we were successful in introducing into a good quality crystal corresponded to a mole ratio of TGFB-TLAFB of 1:1.

### 3.5 TGS-TGSe

Table 6 lists the five growth runs of TGS-TGSe. Each of these homologs grows well in the pure form. However, it proved difficult to grow solid solutions. The TGSe acted much like l-alanine and entered into the TGS lattice with great difficulty. Thus, Run 1-14 with a starting mole ratio of TGS:TGSe of 4:1 produced a crystal whose Curie temperature was  $48.5^{\circ}$ , only slightly lower than that of pure TGS.

Again, the use of doped crystals from a previous run were used as seeds for subsequent runs. This technique was instrumental in obtaining usable crystals. It meant that all growth runs had to be made in series instead of in parallel, thus prolonging the program duration.

TABLE 6

TGS - TGSe GROWTH RUNS

| Run No. | Volume of Solution<br>liters | No. Seeds | Saturation Temp <sup>o</sup> C | Seed Rotation Rate, RPM | pH at 21 <sup>o</sup> C | Length of run days | Mole Ratio TGS : TGSe |
|---------|------------------------------|-----------|--------------------------------|-------------------------|-------------------------|--------------------|-----------------------|
| 1-14    | 6.0                          | 3         | 47.2                           | 10                      | 2.0                     | 63                 | 4:1                   |
| 32-1    | 2.9                          | 3         | 60.2                           | 10                      | 1.97                    | 29                 | 1:1                   |
| 32-2    | 2.9                          | 3         | 59.2                           | 15                      | 1.97                    | 27                 | 1:1                   |
| 33-1    | 2.5                          | 3         | 50                             | 15                      | 2.1                     | 32                 | 1.5:1                 |
| 33-2    | 2.5                          | 3         | 55                             | 15                      | 2.1                     | 46                 | 2:1                   |

NOTES:

1. The seed to shaft distance in each run was 2".
2. Run 1-14 gave 2 good crystals.
3. Run 32-1: crystals strained near seed, but tips usable for seeds. Color, pink.
4. Run 32-2 gave crystals that were cracked, flawed and opaque. Color, pink.
5. Run 33-1: crystals still cracked but less opaque because of lower l-alanine in solution.
6. Run 33-2: crystals still cracked even at lower l-alanine content.



#### 4.0 PREPARATION OF SAMPLES

Crystal samples which cleave easily, such as TGS and its homologs, can be fabricated directly without x-ray orientation. A wet string saw is used to cut the crystal boule to the approximate size and shape desired. The string saw has the advantage over high speed abrasive or diamond wheels of not introducing strains in the crystal, but it does take a much longer time to perform a cut. However, string saws are relatively inexpensive and automatic, so that the cost is low. Since the wet string saw operates by dissolution of the crystal by water, it produces a minimum of work damage on the surface.

Following cutting, it is necessary to grind the surface flat and smooth enough for final polishing. We conventionally use optical grinding machines for this operation, in which the crystal is cemented to a cast iron lap and then moved mechanically over the surface of a rotating flat cast iron lap. Various grades of abrasive powder, such as aluminum oxide lubricated with oil, are used to wet the lap and to provide the grinding action.

Precision polishing of crystals is carried out by first cementing the crystal to a cast iron lap and then working the crystal surface against an optically flat pitch-wax lap. Fine abrasives such as Barnsite (rare earth oxides), and carriers such as ethylene glycol are used. Flatness is periodically checked using a monochromatic light source with an NBS calibrated standard

optical quartz flat. Parallelism is measured with a Nikon autocollimator.

The polished crystals are cleaned with high purity Xylene and are then ready for electroding. Gold electrodes are prepared on the crystal surfaces by vacuum deposition. In the case of samples for relative permittivity measurements, a mask is used during deposition to provide the guard ring configuration.



## 5.0 CRYSTAL MEASUREMENTS

### 5.1 Pyroelectric Coefficient

#### 5.1.1 Byer-Roundy Technique

The pyroelectric coefficient,  $P(T)$  is defined

as:

$$P(T) = \frac{dP_s}{dT}$$

where  $P_s$  is the spontaneous polarization

$$P_s = \frac{Q}{A}$$

where  $Q$  = surface charge on an area  $A$  of the sample

then

$$\frac{dP_s}{dt} = \frac{1}{A} \frac{dQ}{dt} = \frac{I}{A}$$

where  $I$  is the pyroelectric current. Now

$$\left(\frac{dT}{dt}\right)^{-1} \frac{dP_s}{dt} = \frac{dP_s}{dT} = P(T)$$

and

$$P(T) = \frac{I}{A} \left(\frac{dT}{dt}\right)^{-1}$$

In the Byer-Roundy <sup>5</sup> method,  $dT/dt$  is held constant and the pyroelectric current  $I(T)$  is measured as a function of the temperature  $T$ .

The pyroelectric coefficient was measured by the Byer-Roundy method. The thoroughly poled and electroded sample was sealed in a copper block fitted with a thermocouple and hermetically sealed current leads. The copper block was placed in a silicone fluid bath whose temperature was controlled to  $0.05^\circ\text{C}$  by a proportional temperature

controller. The set point of the controller was driven by a timing motor to give a very constant rate of temperature change. A Model 7133A H-P strip chart recorder provided a plot of the temperature as a function of time. Figure 2 shows a typical plot. The rate of temperature change was decreased from  $1^{\circ}\text{C}$  per minute to  $0.4^{\circ}\text{C}$  per minute to improve the linearity by decreasing the lag.

To insure that there were no trapped charges in the sample, the sample was cycled a few times between room temperature and a few degrees above the Curie temperature. The polarity of poling was also reversed to be sure there was no change in pyroelectric coefficient. Finally, the poling voltage was increased from 2000 to 4000 V/cm to be certain of complete poling.

The pyroelectric current was measured by a Keithley Model 616 electrometer and displayed on a Model 4047A H-P X-Y recorder as a function of sample temperature. A typical trace is shown in Figure 3.

#### 5.1.2 TGS

A number of runs were made to standardize the pyroelectric coefficient,  $P(T)$  for TGS. Figure 4 shows that changing the electrode diameter from 3.8 to 9 mm and changing  $dT/dt$  from  $1^{\circ}$  per minute to  $0.4^{\circ}$  per minute did not change  $P(T)$ . Figure 5 compares average INRAD results with those reported by Isomet and Keve<sup>4</sup>. The agreement is good.

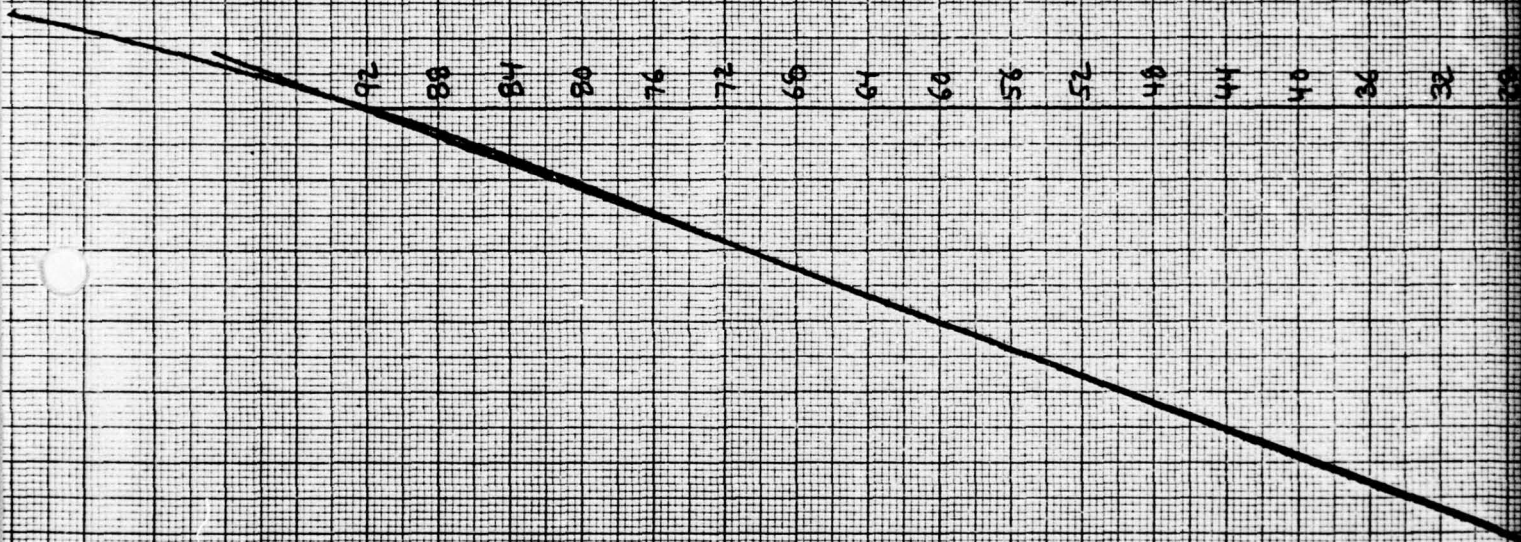


THERMOCOUPLE OUTPUT VS TIME

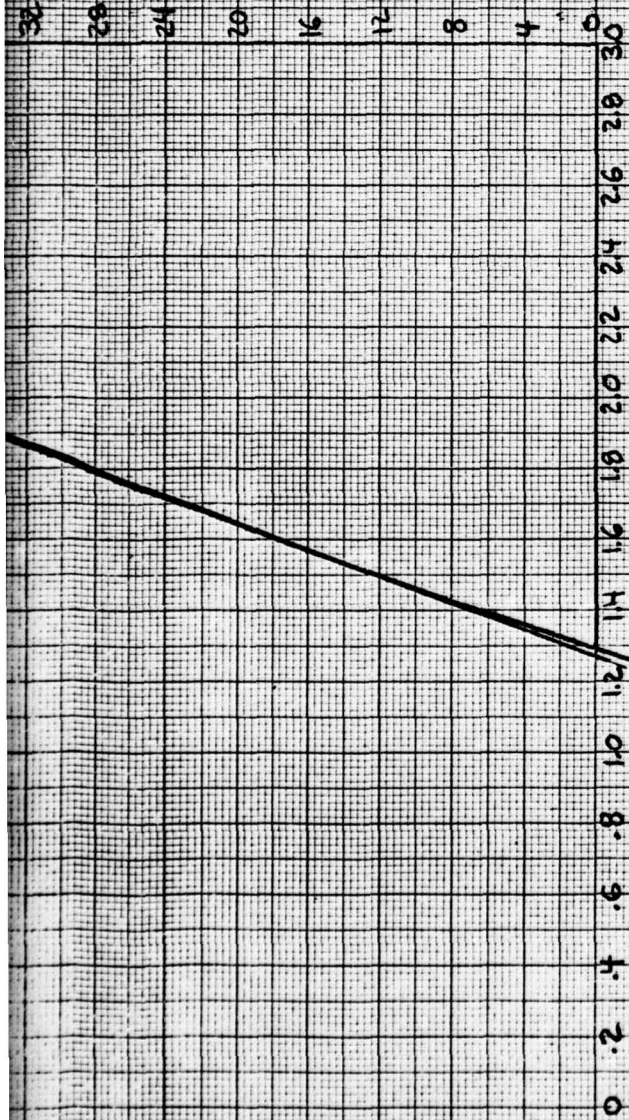
CHART SPEED = 15 CM/MIN

5 MV SPAN (0.2 MV/CM)

$$\text{SLOPE} = \frac{\Delta X}{\Delta Y} = \frac{39.8}{92} = .433 \text{ } ^\circ\text{C}/\text{MIN.}$$







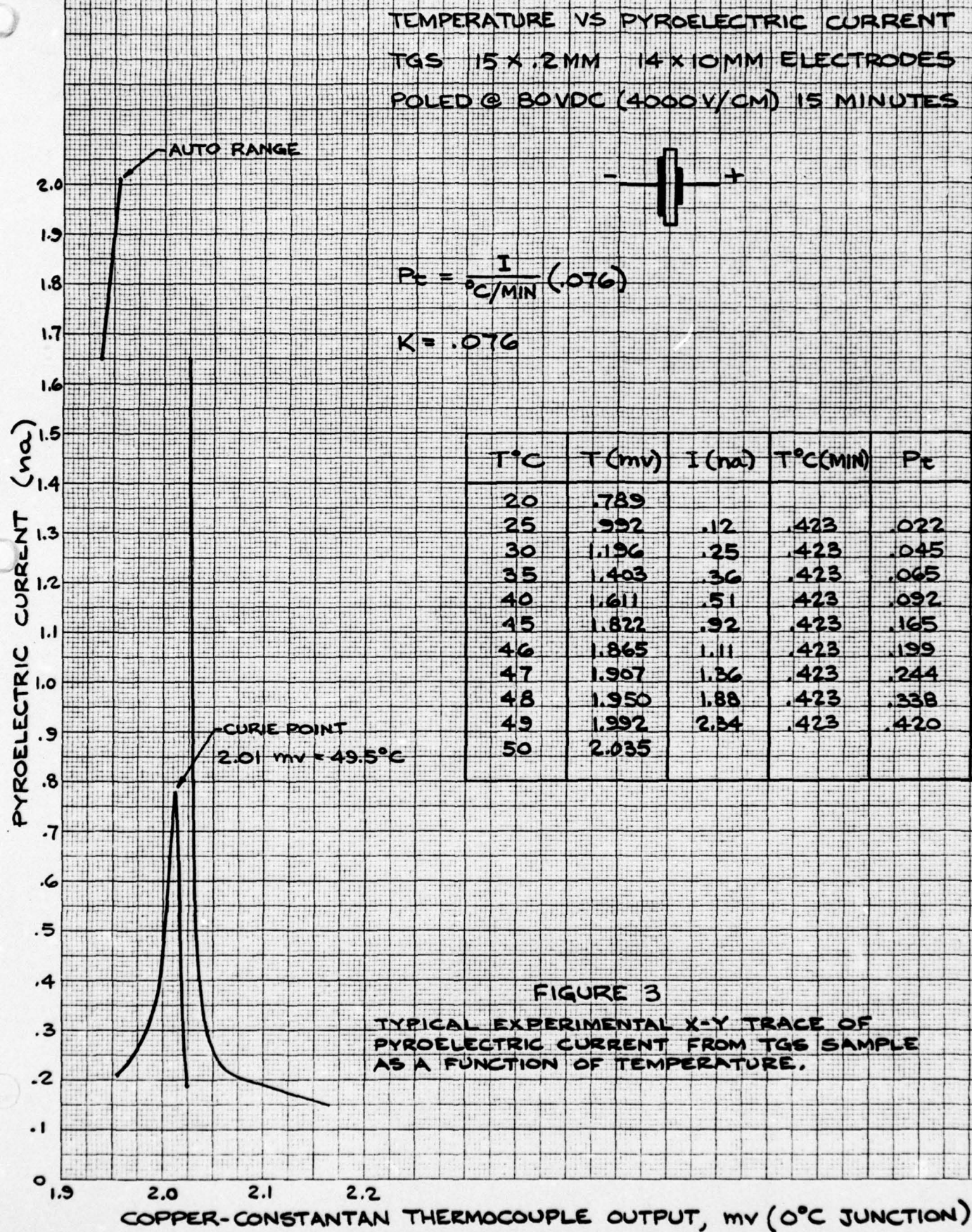
(mV)

1.29 mV = 32.2°C      3.0 mV = 72°C

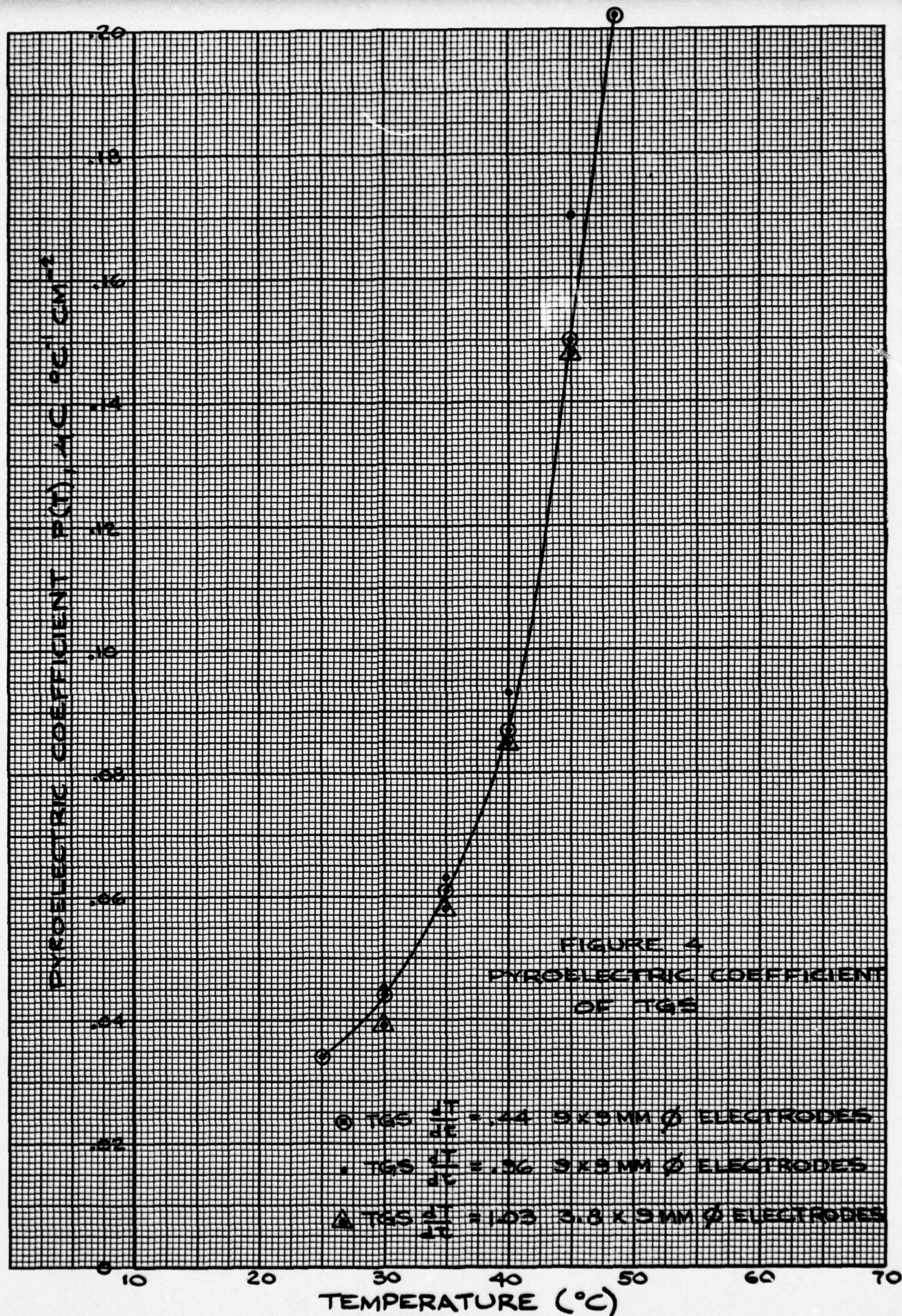
Cu/Cs THERMOCOUPLE OUTPUT (mV) 0°C JUNCTION

FIGURE 2  
Linearity of Temperature Drive for Byer-Roundy Pyroelectric Measurements

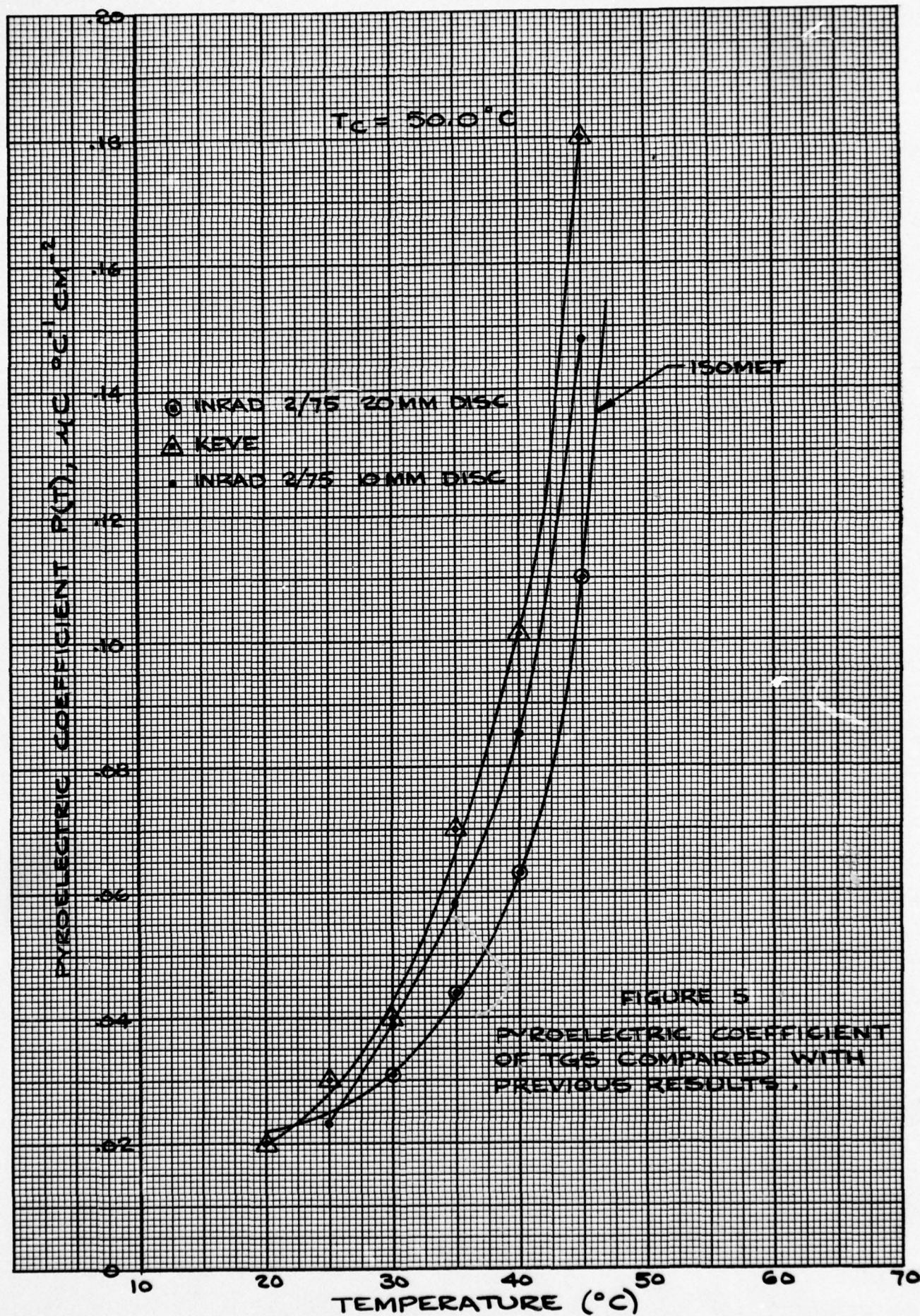












### 5.1.3 TGFB and D-TGFB

TGFB and D-TGFB samples were run and rerun many times during which the poling temperature was varied from 20° to 60°, the poling voltage was varied from 1000 to 4000 volts per cm, the poling direction was reversed, and the poling time was varied from 15 minutes to 17 hours. The results are shown in Figures 6 and 7. Higher poling voltages, temperatures, and poling time did not materially affect the results shown.

Figure 8 gives the pyroelectric coefficient,  $P(T)$ , as a function of temperature for TGS, TGFB, and D-TGFB. The coefficients of TGFB and D-TGFB do not differ very much, but both are much lower than  $P(T)$  for pure TGS.

### 5.1.4 l-Alanine Doped TGS

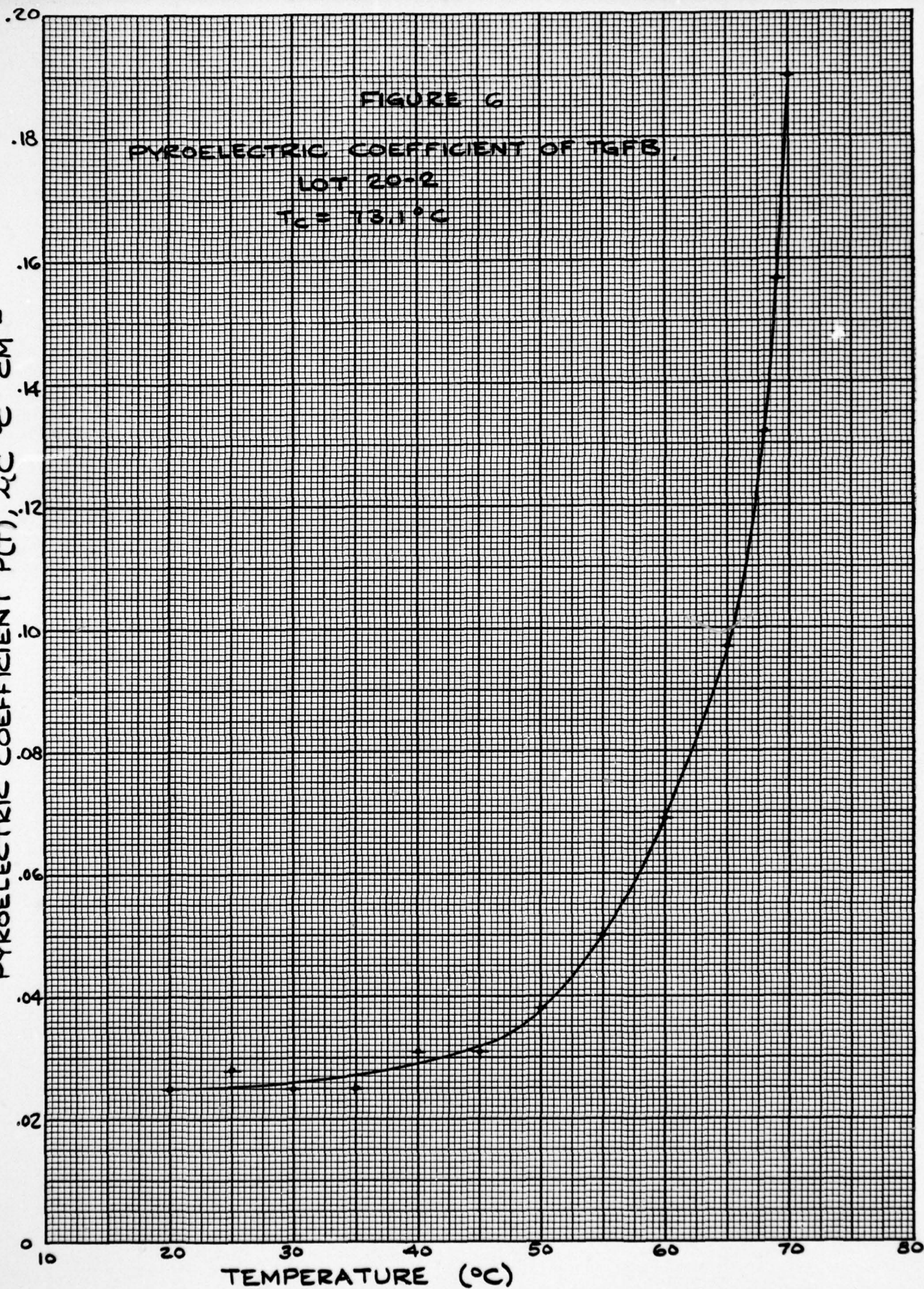
Figure 9 shows the pyroelectric coefficient as a function of temperature for TGS/TLAS with a mole ratio of 1:1. Figure 10 compares  $P(T)$  for TGS/TLAS with that of pure TGS. No significant difference in  $P(T)$  was observed as a result of the alanine doping.

In Figure 11  $P(T)$  has been plotted as a function of  $T$  through the Curie point. There is no sharp Curie point. Instead,  $P(T)$  exhibits a broadened transition as was observed by Keve<sup>4</sup>.



K&E 20 X 20 TO THE INCH 46 1242  
7 X 10 INCHES  
MADE IN U.S.A.  
KEUFFEL & ESSER CO.

PYROELECTRIC COEFFICIENT  $P(T)$ ,  $\mu C \text{ cm}^{-2}$





K-E 20 X 20 TO THE INCH 46 1242  
7 X 10 INCHES  
MADE IN U.S.A.  
KEUFFEL & ESSER CO.

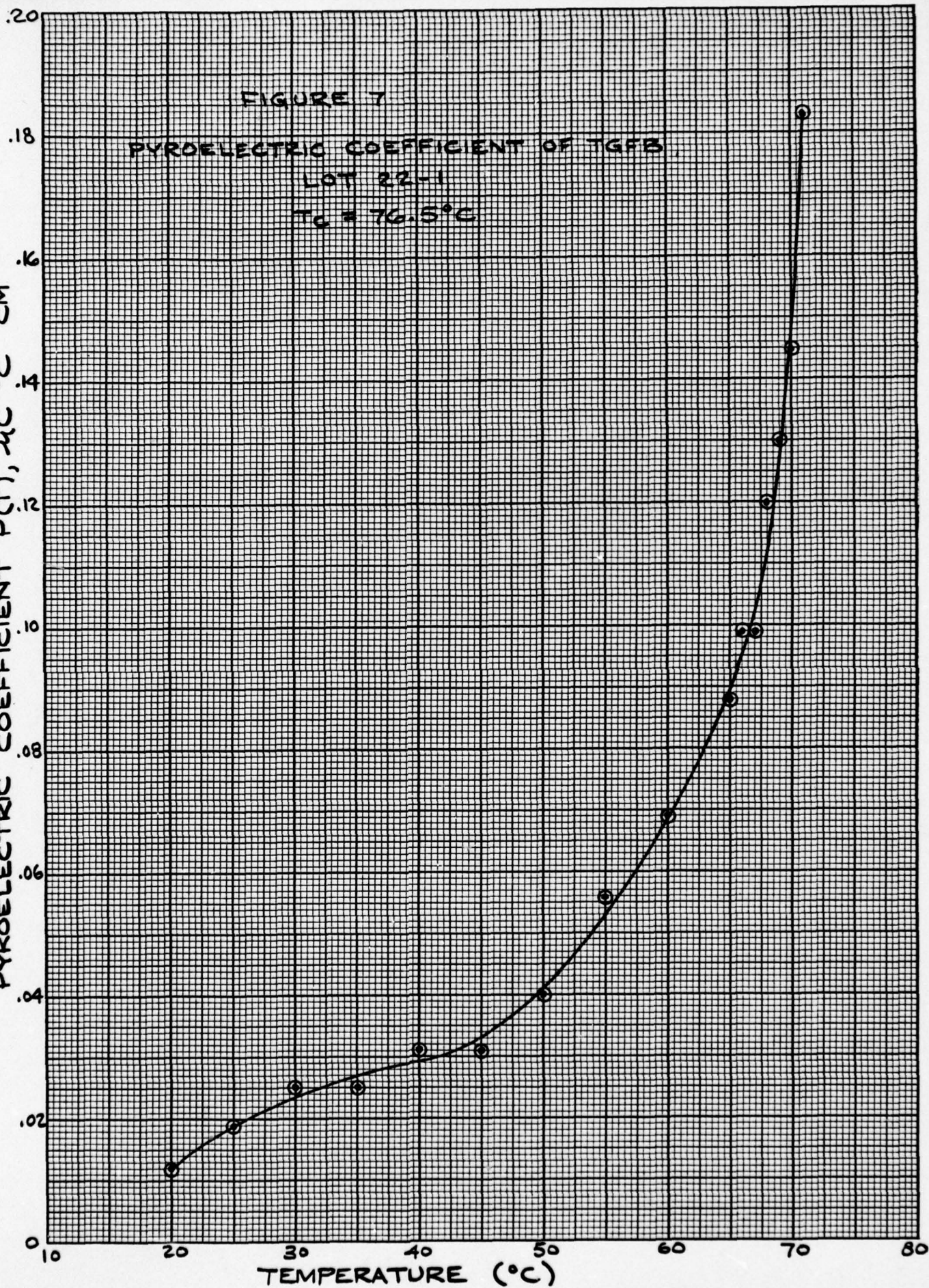
PYROELECTRIC COEFFICIENT  $P(T)$ ,  $\mu\text{C } ^\circ\text{C}^{-1} \text{cm}^{-2}$

FIGURE 7

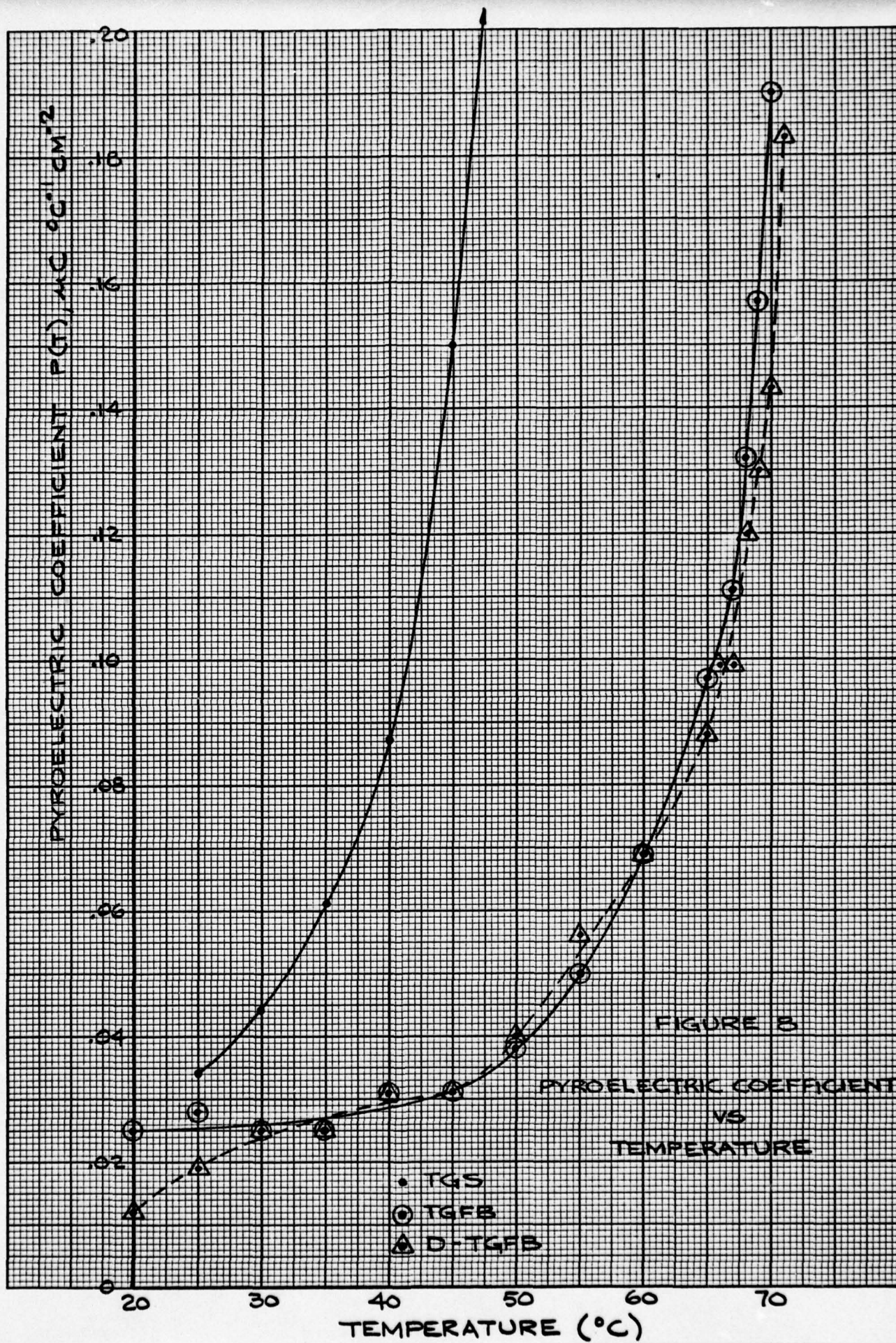
PYROELECTRIC COEFFICIENT OF TGFB

LOT 22-1

$T_C = 70.5^\circ\text{C}$

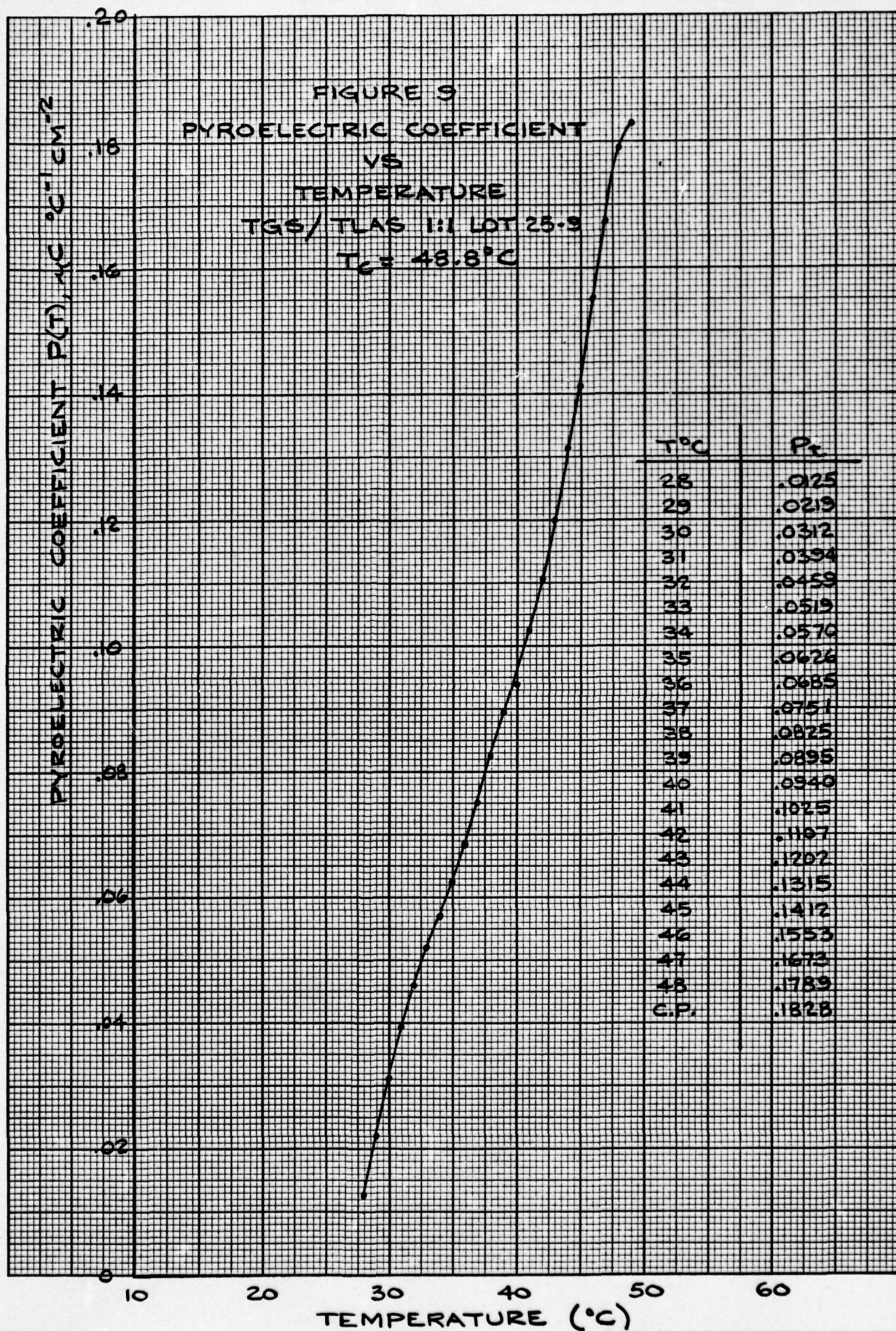




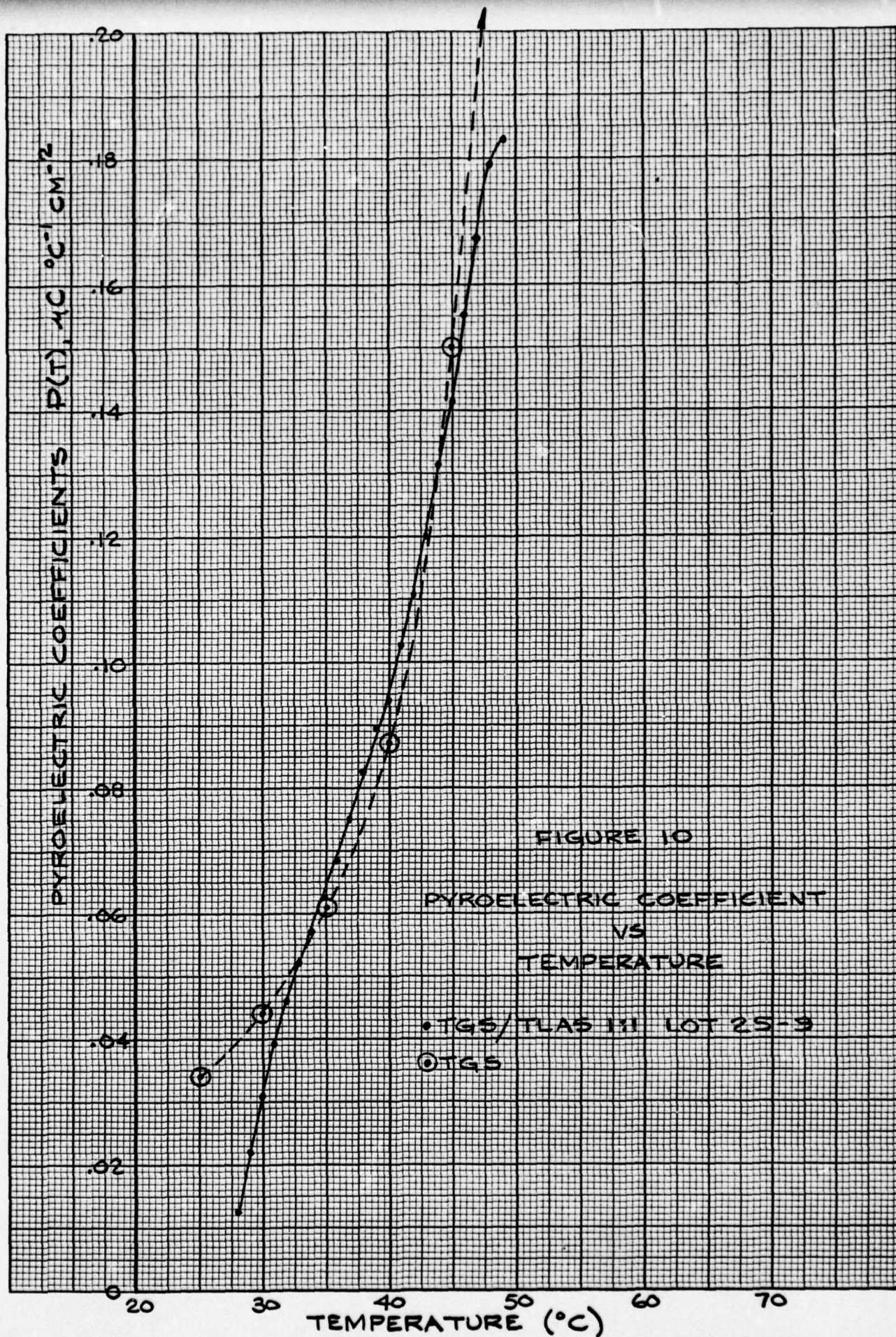




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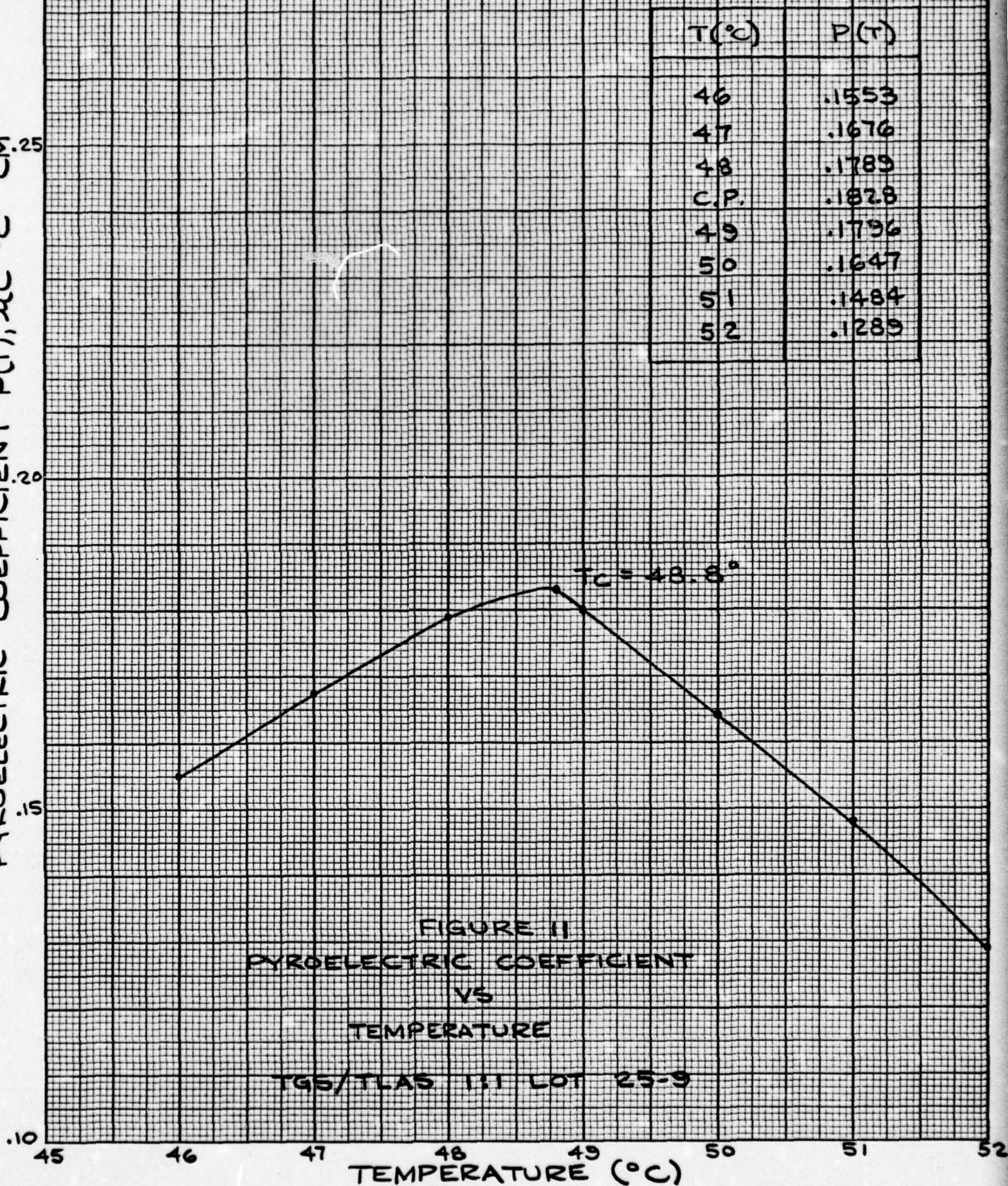






K&E 20 X 20 TO THE INCH 46 1242  
7 X 10 INCHES  
MADE IN U.S.A.  
KEUFFEL & ESSER CO.

PYROELECTRIC COEFFICIENT  $P(T)$ ,  $\mu C \text{ } ^\circ C^{-1} \text{ CM}^{-2}$





#### 5.1.5 1-Alanine Doped TGFB

Measurements of  $P(T)$  for two different 1-alanine doping levels of TGFB are shown in Figures 12 and 13, while Figure 14 compares two doped TGFB crystals with pure TGFB. No significant differences in  $P(T)$  can be attributed to the 1-alanine doping.

In Figure 15 is plotted  $P(T)$  as a function of temperature through the Curie temperature of TGFB/TLAFB grown from a solution with a mole ratio of 1:1. As in the case of TGS/TLAS the curve is broadened at the Curie point as a result of the 1-alanine doping.

#### 5.1.6 TGS-TGSe

Only one mole ratio of TGS/TGSe produced stable enough crystals for measurements. Samples of the other mole ratios cracked in fabrication, probably because of strain. Figure 16 presents  $P(T)$  for TGS/TGSe grown from a solution having a mole ratio of TGS:TGSe of 4:1. Figure 17 compares this sample of TGS/TGSe with pure TGS. The Se doping did not materially affect the pyroelectric coefficient. In Figure 18  $P(T)$  is plotted as a function of temperature through the Curie point. The curve is broadened at the peak just as in the case of the 1-alanine doped TGS and TGFB. The TGS/TGSe crystal performed as if the Se were a dopant rather than as a solid solution of TGS and TGSe as had been expected.

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FIGURE 12

PYROELECTRIC COEFFICIENT  
VS

TEMPERATURE

TGFB/TLAFB 1.5:1 LOT 26-13

$T_C = 75.7^\circ\text{C}$

PYROELECTRIC COEFFICIENT  $P(T)$ ,  $\mu\text{C } ^\circ\text{C}^{-1} \text{CM}^{-2}$

| $T^\circ\text{C}$ | $P_c$ |
|-------------------|-------|
| 22                | .0048 |
| 25                | .0109 |
| 30                | .0167 |
| 35                | .0208 |
| 40                | .0251 |
| 45                | .0273 |
| 50                | .0323 |
| 55                | .0410 |
| 60                | .0557 |
| 65                | .0815 |
| 70                | .1409 |
| 75                | .8181 |
| C.P.              | 6.046 |

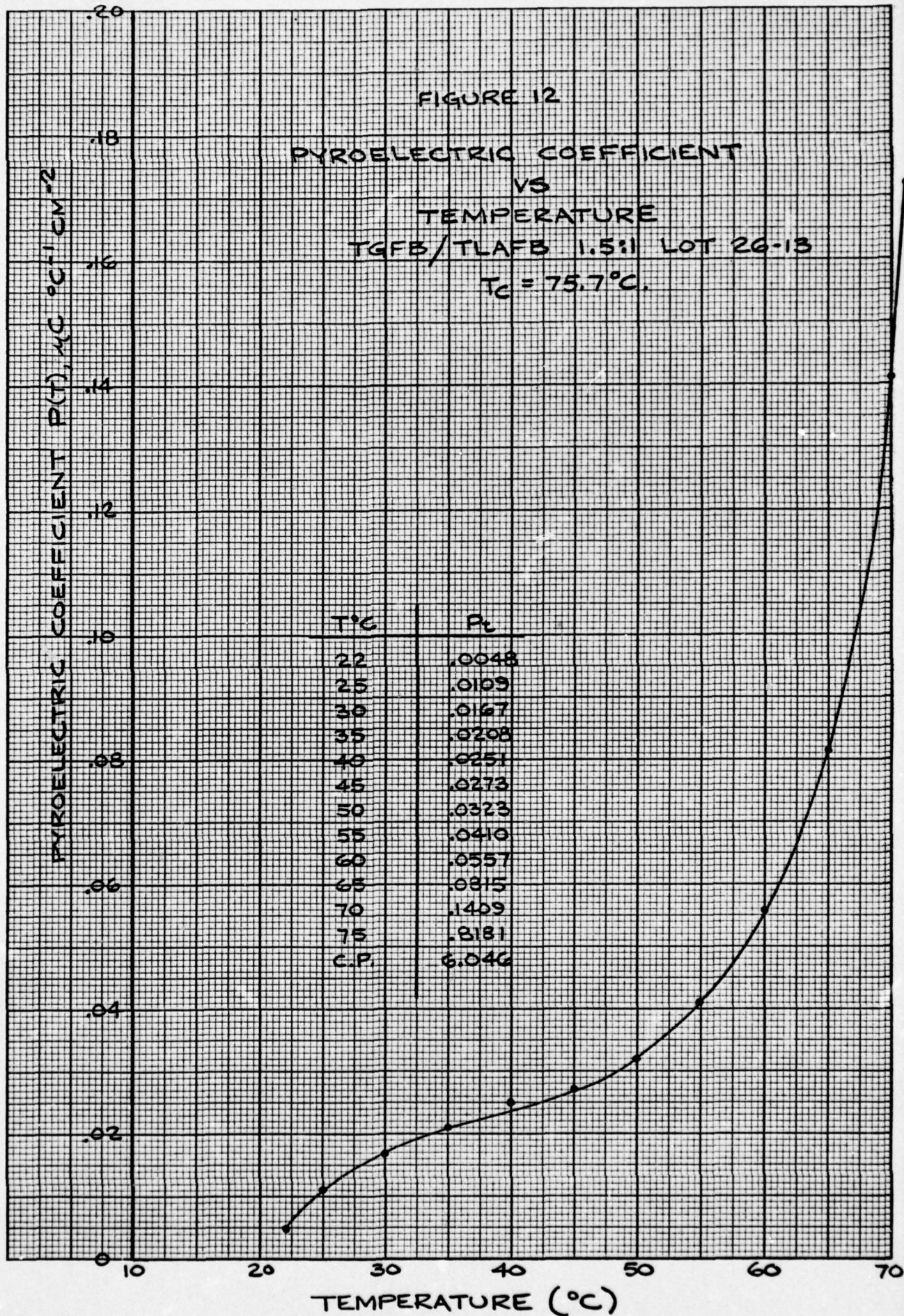


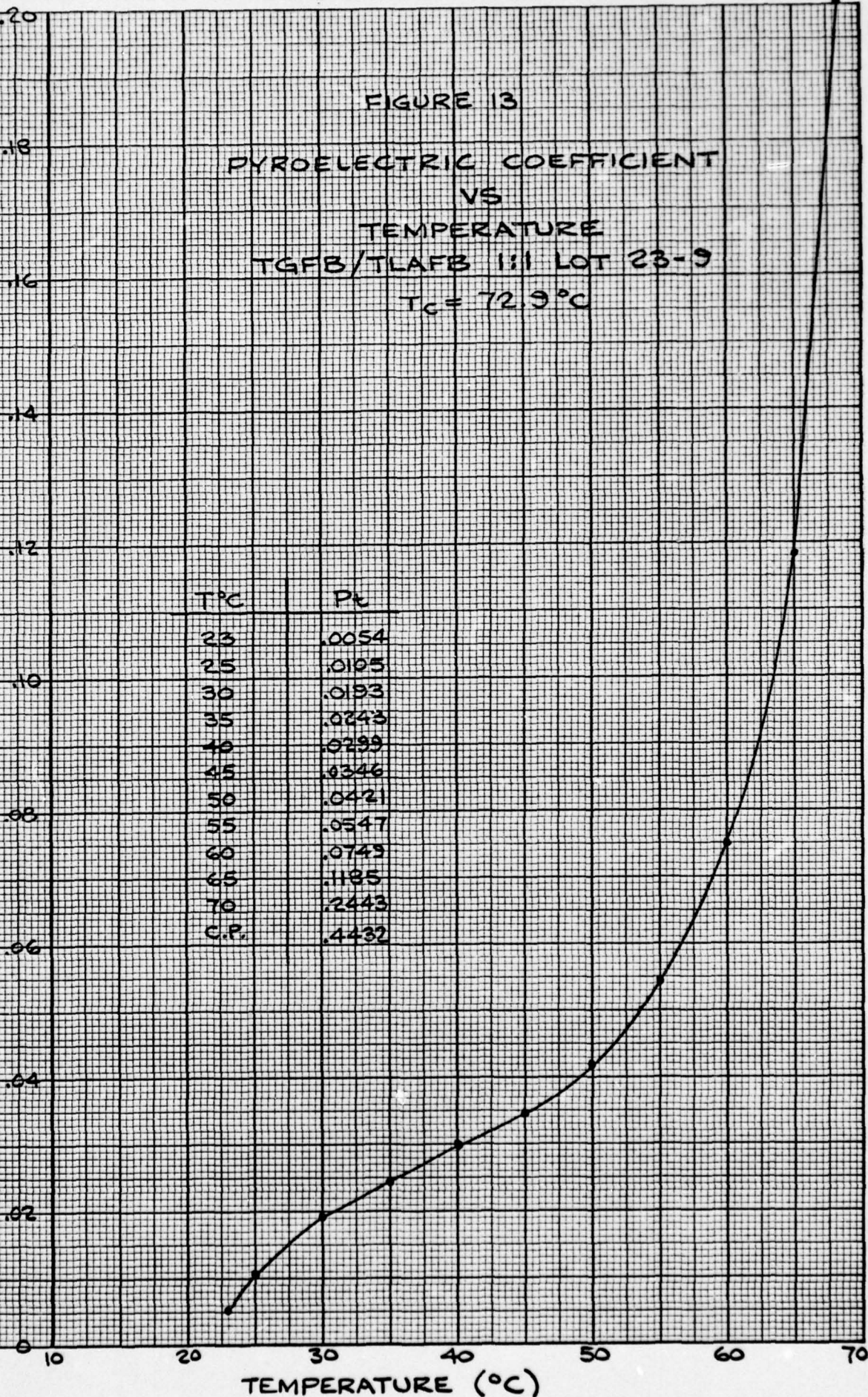


FIGURE 13

PYROELECTRIC COEFFICIENT  
VS  
TEMPERATURE  
TGFB/TLAFB 1:1 LOT 23-9  
 $T_C = 72.9^\circ\text{C}$

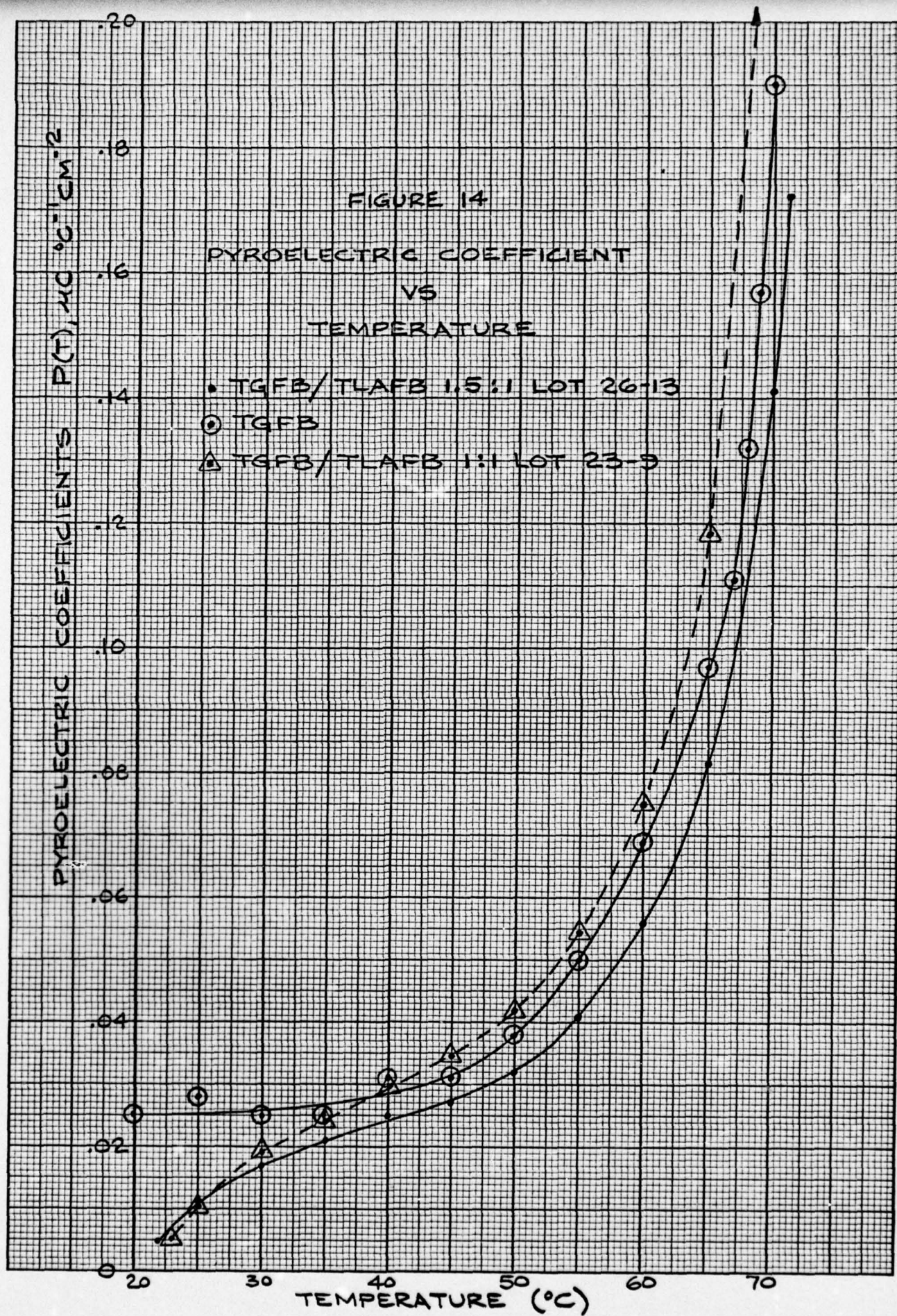
PYROELECTRIC COEFFICIENT  $P(T)$ ,  $\mu\text{C } ^\circ\text{C}^{-1}\text{CM}^{-2}$

| $T^\circ\text{C}$ | $P_T$ |
|-------------------|-------|
| 23                | .0054 |
| 25                | .0105 |
| 30                | .0193 |
| 35                | .0243 |
| 40                | .0299 |
| 45                | .0346 |
| 50                | .0421 |
| 55                | .0547 |
| 60                | .0749 |
| 65                | .1185 |
| 70                | .2443 |
| C.P.              | .4432 |



TEMPERATURE ( $^\circ\text{C}$ )







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7 X 10 INCHES  
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PYROELECTRIC COEFFICIENT  $P(T)$   $\mu C \text{ } ^\circ C^{-1} \text{ CM}^{-2}$

| T( $^\circ C$ ) | P(T)  |
|-----------------|-------|
| 70              | .2443 |
| 71              | .3001 |
| 72              | .3787 |
| C.P.            | .4432 |
| 73              | .4423 |
| 74              | .2870 |
| 75              | .1789 |
| 76              | .1108 |

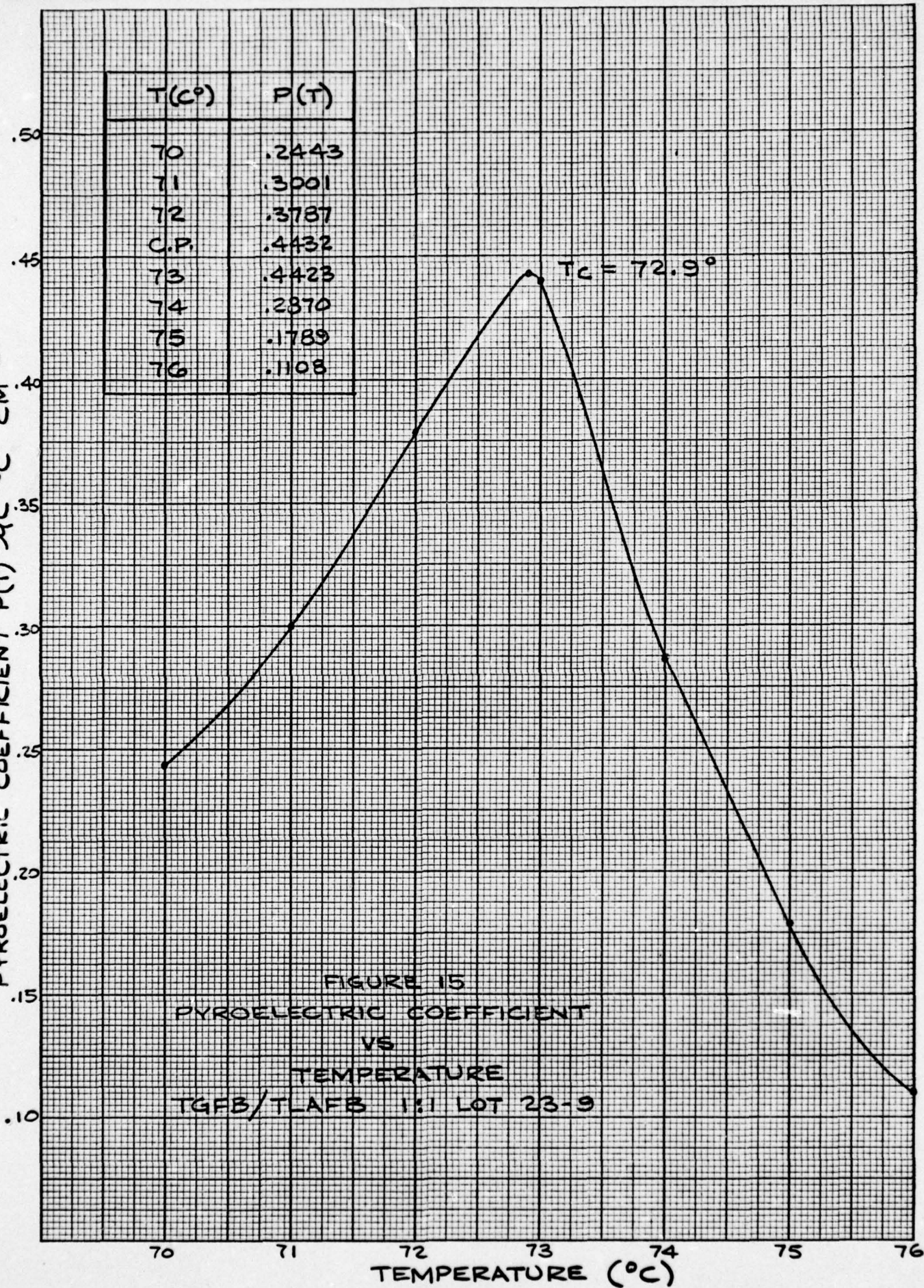
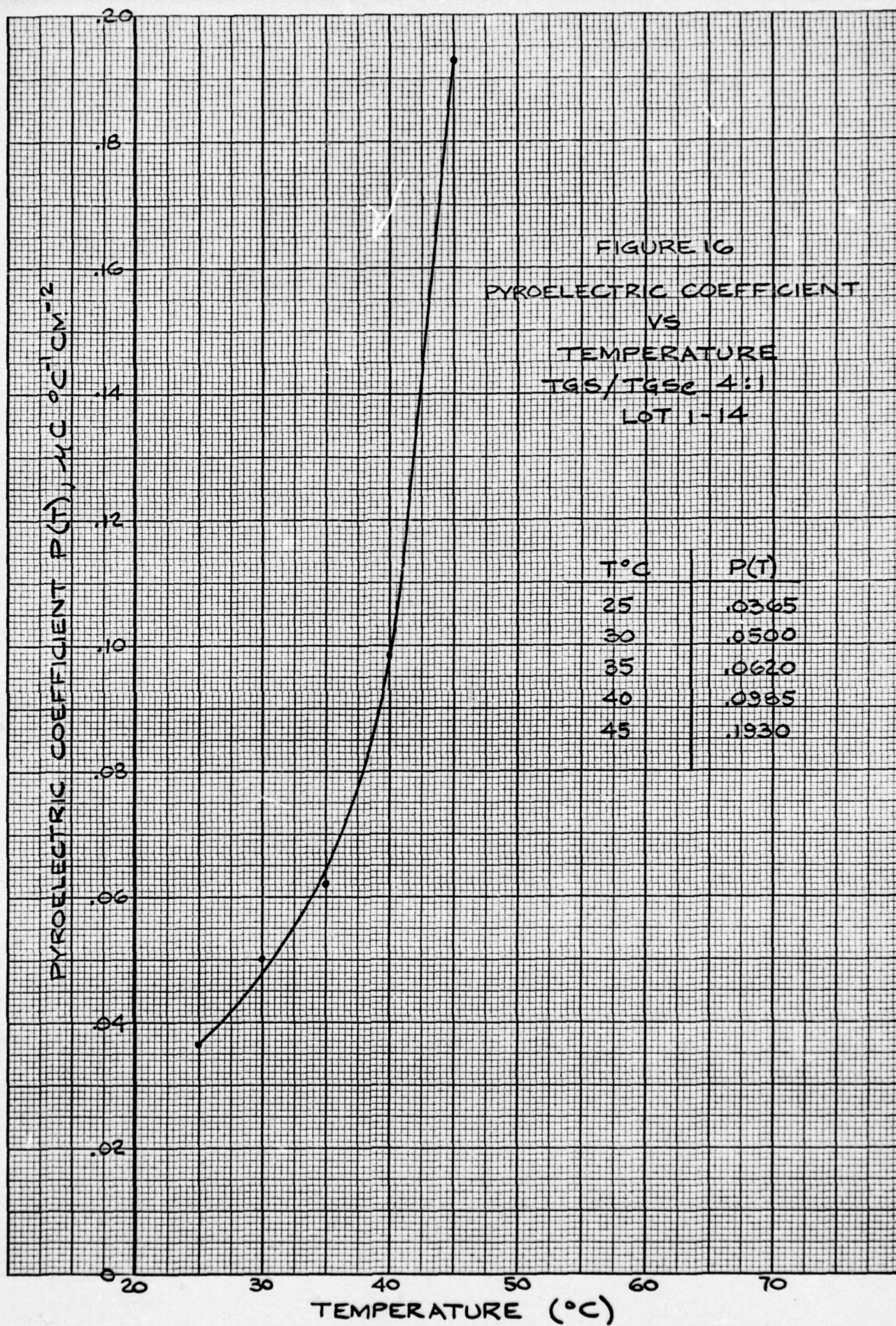


FIGURE 15  
PYROELECTRIC COEFFICIENT  
VS  
TEMPERATURE  
TGFB/TLAFB 1:1 LOT 23-9

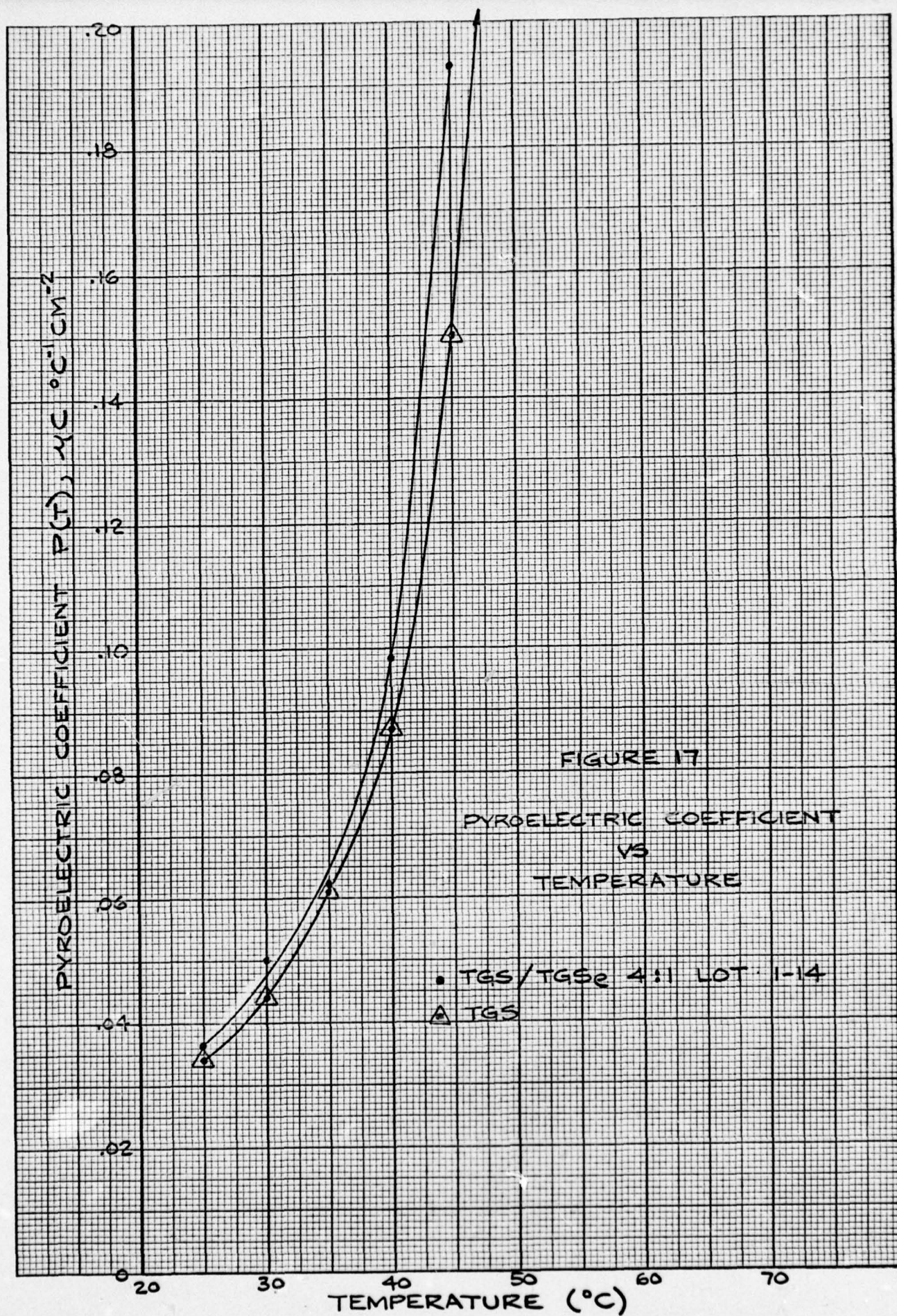


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K&E 20 X 20 TO THE INCH 46 1242  
7 X 10 INCHES  
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PYROELECTRIC COEFFICIENT  $P(T)$   $\mu\text{C } ^\circ\text{C}^{-1} \text{cm}^{-2}$

| T( $^\circ\text{C}$ ) | P(T)  |
|-----------------------|-------|
| 45                    | .2331 |
| 46                    | .2979 |
| 47                    | .4752 |
| C.P.                  | .8788 |
| 48                    | .3931 |
| 49                    | .0243 |
| 50                    | .0178 |

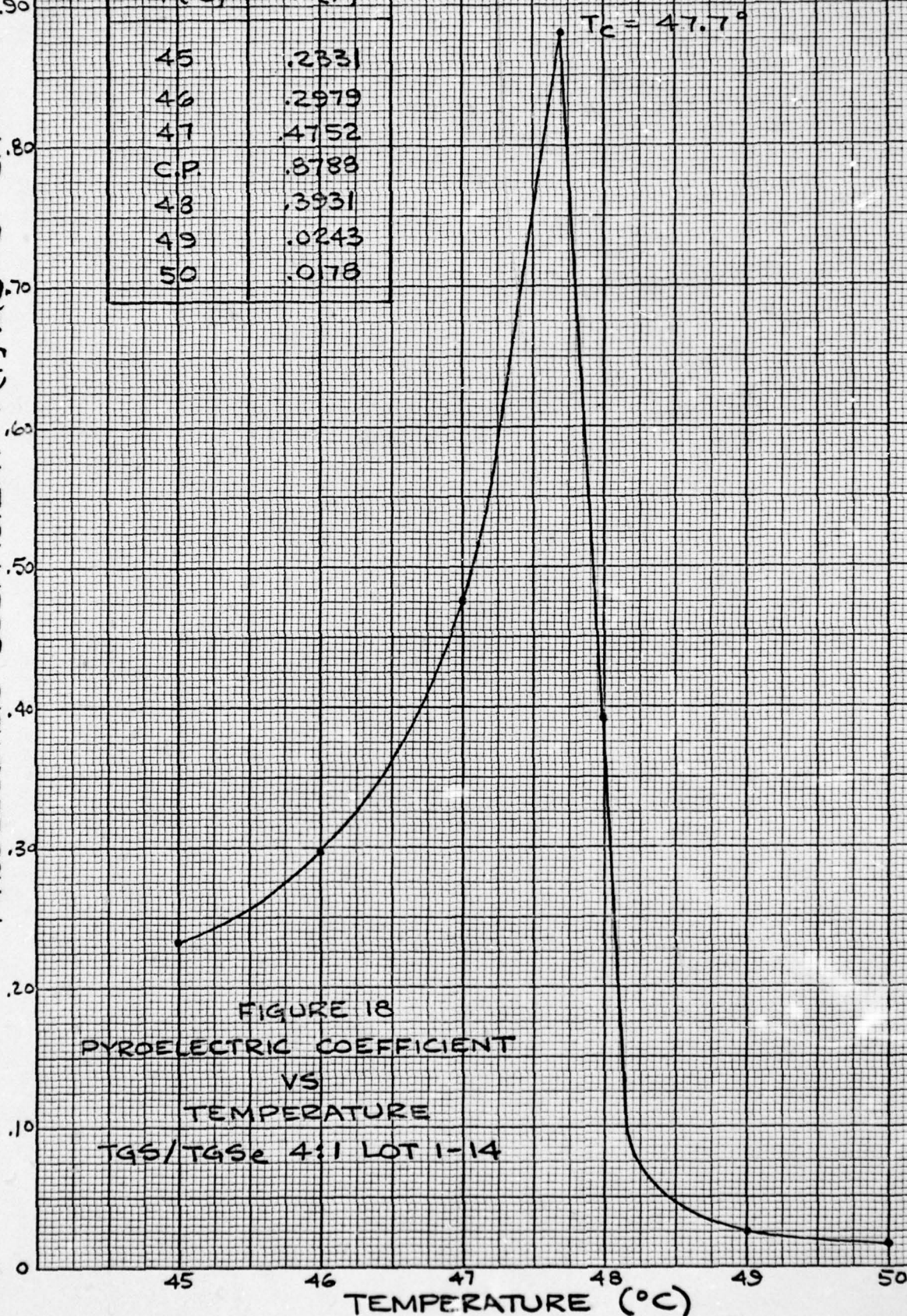


FIGURE 18  
PYROELECTRIC COEFFICIENT  
VS  
TEMPERATURE  
TGS/TGSe 4:1 LOT 1-14



## 5.2 Dielectric Constant

### 5.2.1 Measurement Procedure

Standard samples were 15mm in diameter and were electroded in a guard ring configuration<sup>6</sup> by a vacuum deposition of gold. The vacuum capacitance is calculated from the formula:

$$C_v = \epsilon_0 \frac{A}{t}$$

Where A is a parameter that depends on the guard ring dimensions, the relative permittivity  $\epsilon_r$  is calculated from:

$$\epsilon_r = \frac{C_p}{C_v} \quad (\text{meas.})$$

A General Radio capacitance bridge is used to measure the series equivalent capacitance,  $C_s$  and the loss tangent  $\tan \delta$  from which  $C_p$  is obtained

$$C_p = \frac{C_s}{1 + (\tan \delta)^2}$$

The electroded sample was poled and then sealed in a aluminum container which is immersed in a bath whose temperature is controlled to 0.05°C with a proportional temperature controller. Measurements of  $C_s$  and  $\tan \delta$  are made at various temperatures after the sample has reached equilibrium.

Measurements were made with and without a bias voltage to determine if the bias produced any change in the relative permittivity. No significant changes were observed.

## 5.2.2 Relative Permittivity Data

### 5.2.2.1 TGS, TGFB, and D-TGFB

Figures 19, 20, and 21 show  $\epsilon_r$  as a function of temperature for TGS, TGFB, and D-TGFB. In each case  $\epsilon_r$  was measured with and without a bias field to determine if the bias would affect the results. No significant effect of bias was observed. Figure 22 compares  $\epsilon_r$  as a function of T for TGS, TGFB, and D-TGFB. Deuteration of TGFB markedly reduced the relative permittivity of TGFB. Both TGFB and D-TGFB have a much lower relative permittivity than TGS.

### 5.2.2.2 1-Alanine Doped TGS

The relative permittivity of TGS/TLAS 1:1 is plotted as a function of temperature in Figure 23, and is compared with pure TGS in Figure 24. Although TGS/TLAS exhibits lower values of  $\epsilon_r$ , more data is needed to establish that the results are significant.

### 5.2.2.3 1-Alanine Doped TGFB

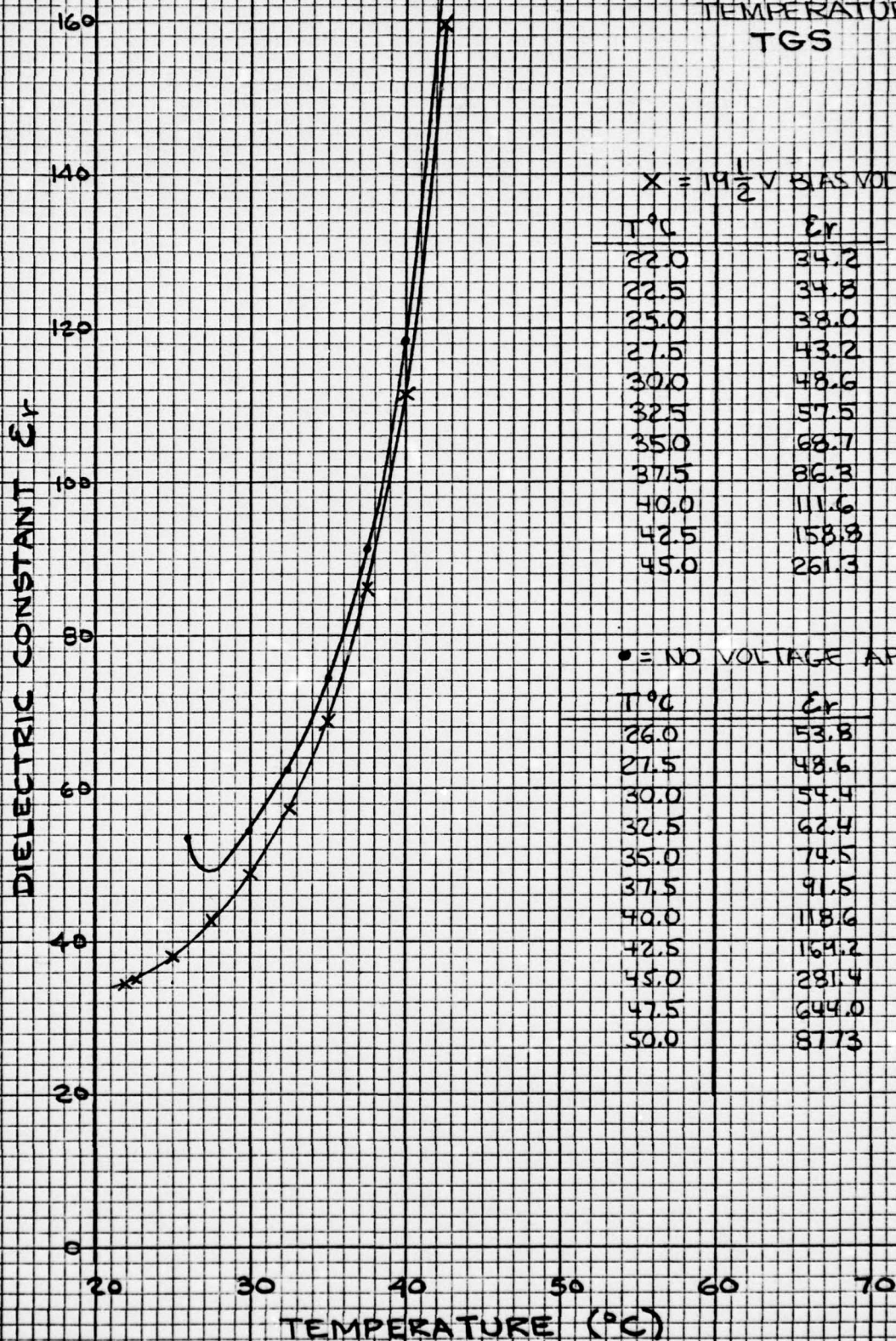
Figures 25, 26, and 27 gives results for two different 1-alanine doping levels of TGFB and a comparison with pure TGFB.

### 5.2.2.4 TGS-TGSe

The relative permittivity of TGS/TGSe 4:1 is plotted in Figure 28 and compared with TGS in Figure 29. The selenium doping produced no significant effect on the relative permittivity.



FIGURE 19  
DIELECTRIC CONSTANT  
VS  
TEMPERATURE  
TGS



X = 19  $\frac{1}{2}$  V BIAS VOLTAGE APPLIED

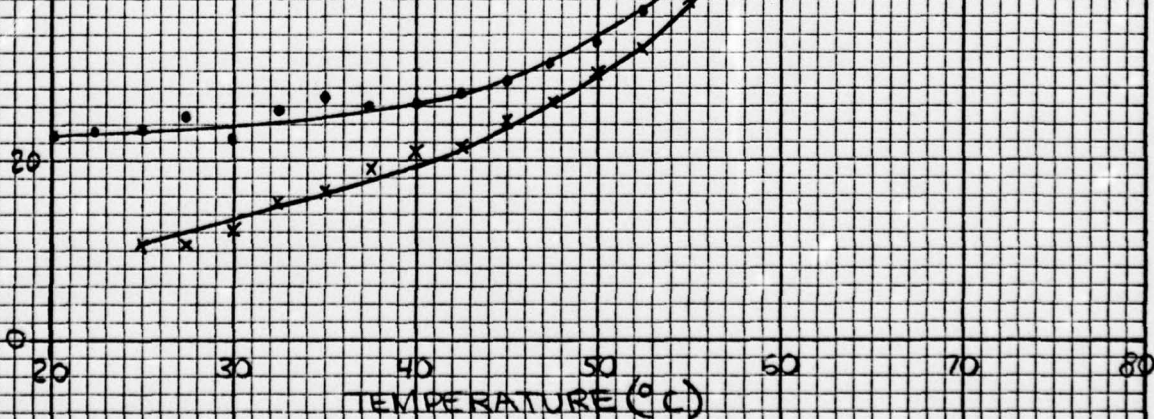
| T $^{\circ}\text{C}$ | $\epsilon_r$ |
|----------------------|--------------|
| 22.0                 | 34.2         |
| 22.5                 | 34.8         |
| 25.0                 | 38.0         |
| 27.5                 | 43.2         |
| 30.0                 | 48.6         |
| 32.5                 | 57.5         |
| 35.0                 | 68.7         |
| 37.5                 | 86.3         |
| 40.0                 | 111.6        |
| 42.5                 | 158.8        |
| 45.0                 | 261.3        |

• = NO VOLTAGE APPLIED

| T $^{\circ}\text{C}$ | $\epsilon_r$ |
|----------------------|--------------|
| 26.0                 | 53.8         |
| 27.5                 | 48.6         |
| 30.0                 | 54.4         |
| 32.5                 | 62.4         |
| 35.0                 | 74.5         |
| 37.5                 | 91.5         |
| 40.0                 | 118.6        |
| 42.5                 | 164.2        |
| 45.0                 | 281.4        |
| 47.5                 | 644.0        |
| 50.0                 | 877.3        |

| • = NO VOLTAGE APPLIED |                | X = 19½ V BIAS VOLTAGE APPLIED |                |
|------------------------|----------------|--------------------------------|----------------|
| T °C                   | ε <sub>r</sub> | T °C                           | ε <sub>r</sub> |
| 20.0                   | 22.9           | 25.0                           | 15.5           |
| 22.5                   | 23.0           | 27.5                           | 15.5           |
| 25.0                   | 23.7           | 30.0                           | 16.1           |
| 27.5                   | 24.5           | 32.5                           | 19.6           |
| 30.0                   | 27.1           | 35.0                           | 18.4           |
| 32.5                   | 25.9           | 37.5                           | 19.3           |
| 35.0                   | 27.0           | 40.0                           | 20.1           |
| 37.5                   | 26.2           | 42.5                           | 21.6           |
| 40.0                   | 26.7           | 45.0                           | 24.5           |
| 42.5                   | 27.6           | 47.5                           | 26.5           |
| 45.0                   | 29.1           | 50.0                           | 29.9           |
| 47.5                   | 31.0           | 52.5                           | 32.5           |
| 50.0                   | 33.4           | 55.0                           | 38.0           |
| 52.5                   | 36.3           | 57.5                           | 43.4           |
| 55.0                   | 41.1           | 60.0                           | 50.6           |
| 57.5                   | 47.5           | 62.5                           | 64.5           |
| 60.0                   | 59.0           | 65.0                           | 82.0           |
| 62.5                   | 67.0           | 67.5                           | 110            |
| 65.0                   | 84.0           | 70.0                           | 207            |
| 67.5                   | 116            |                                |                |
| 70.0                   | 185            |                                |                |

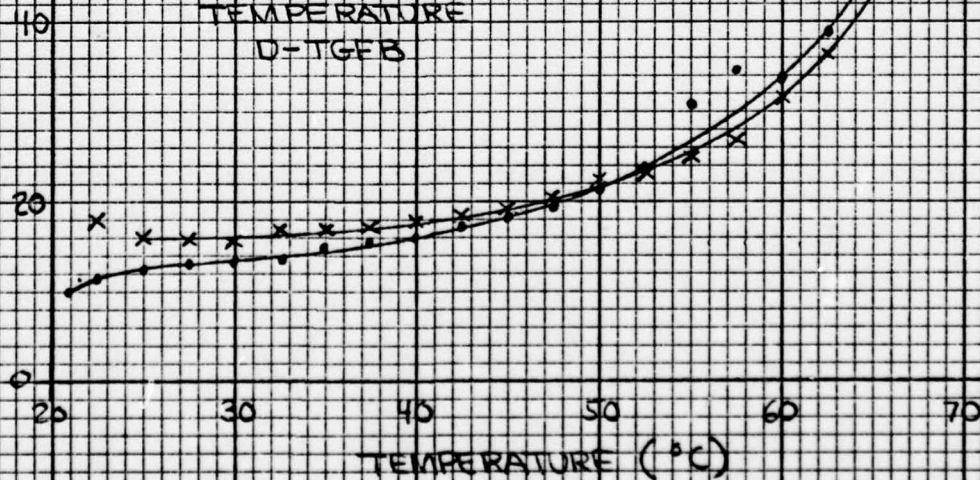
FIGURE 20  
DIELECTRIC CONSTANT  
VS  
TEMPERATURE  
TGFB

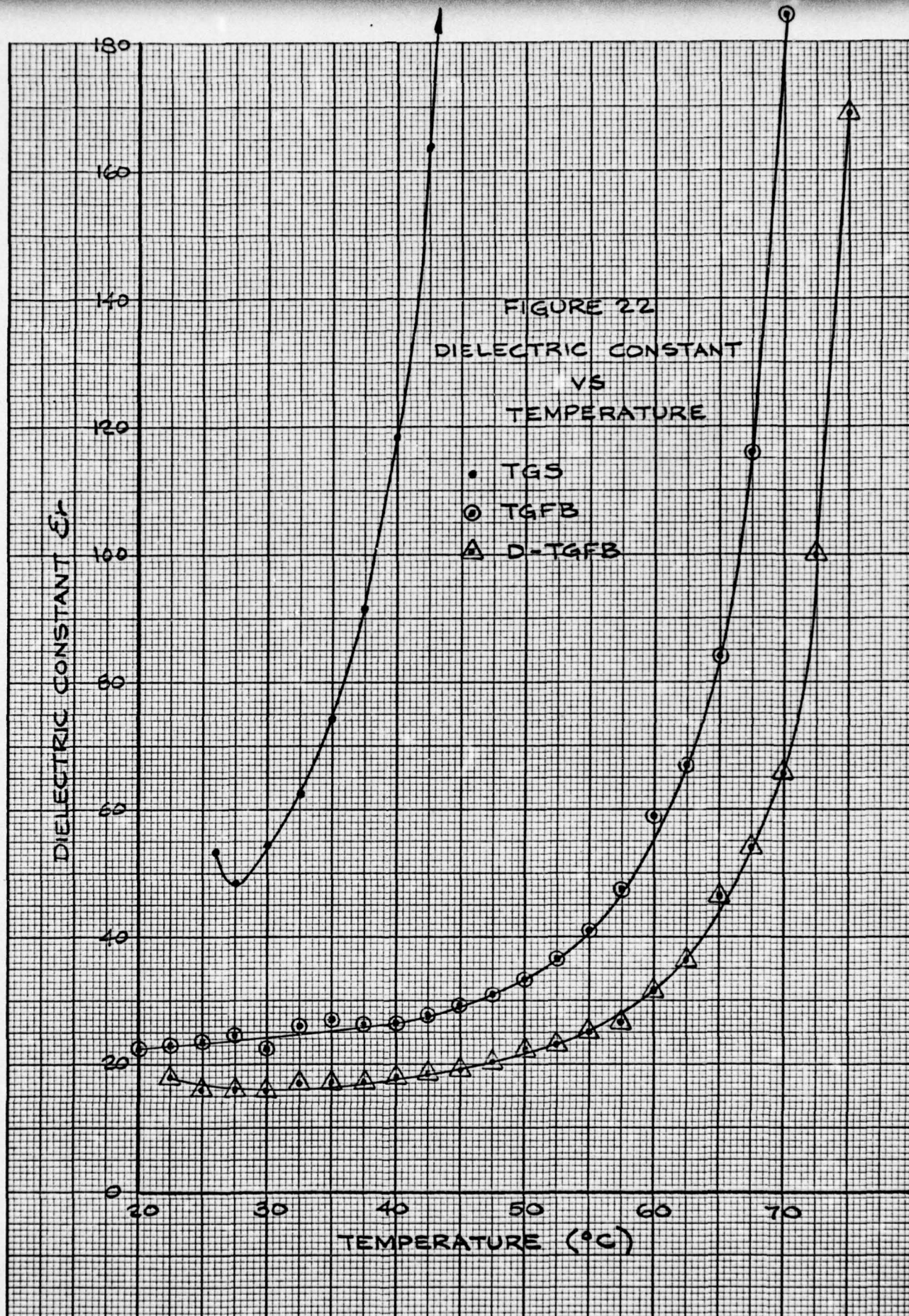




| • = NO VOLTAGE APPLIED |                | X = 19½ V BIAS VOLTAGE APPLIED |                |
|------------------------|----------------|--------------------------------|----------------|
| T °C                   | ε <sub>r</sub> | T °C                           | ε <sub>r</sub> |
| 21.0                   | 10.1           | 22.5                           | 17.8           |
| 21.5                   | 11.5           | 25.0                           | 16.0           |
| 22.5                   | 11.8           | 27.5                           | 15.8           |
| 25.0                   | 12.2           | 30.0                           | 15.5           |
| 27.5                   | 12.7           | 32.5                           | 16.7           |
| 30.0                   | 13.2           | 35.0                           | 16.7           |
| 32.5                   | 13.5           | 37.5                           | 16.9           |
| 35.0                   | 14.7           | 40.0                           | 17.5           |
| 37.5                   | 15.3           | 42.5                           | 18.1           |
| 40.0                   | 16.1           | 45.0                           | 19.0           |
| 42.5                   | 17.3           | 47.5                           | 20.4           |
| 45.0                   | 18.1           | 50.0                           | 22.1           |
| 47.5                   | 19.6           | 52.5                           | 22.7           |
| 50.0                   | 21.3           | 55.0                           | 24.7           |
| 52.5                   | 23.5           | 57.5                           | 26.5           |
| 55.0                   | 31.1           | 60.0                           | 31.6           |
| 57.5                   | 34.5           | 62.5                           | 36.2           |
| 60.0                   | 33.4           | 65.0                           | 46.9           |
| 62.5                   | 38.8           | 67.5                           | 54.1           |
| 65.0                   | 47.2           | 70.0                           | 65.6           |
| 67.5                   | 57.0           | 72.5                           | 100.0          |
| 70.0                   | 83.5           | 75.0                           | 169.2          |
| 72.5                   | 126            |                                |                |
| 75.0                   | 261            |                                |                |
| 77.5                   | 4313           |                                |                |

FIGURE 21  
DIELECTRIC CONSTANT  
VS  
TEMPERATURE  
D-TGFB







DIELECTRIC CONSTANT  $\epsilon_r$

160

140

120

100

80

60

40

20

0

20

30

40

50

60

70

80

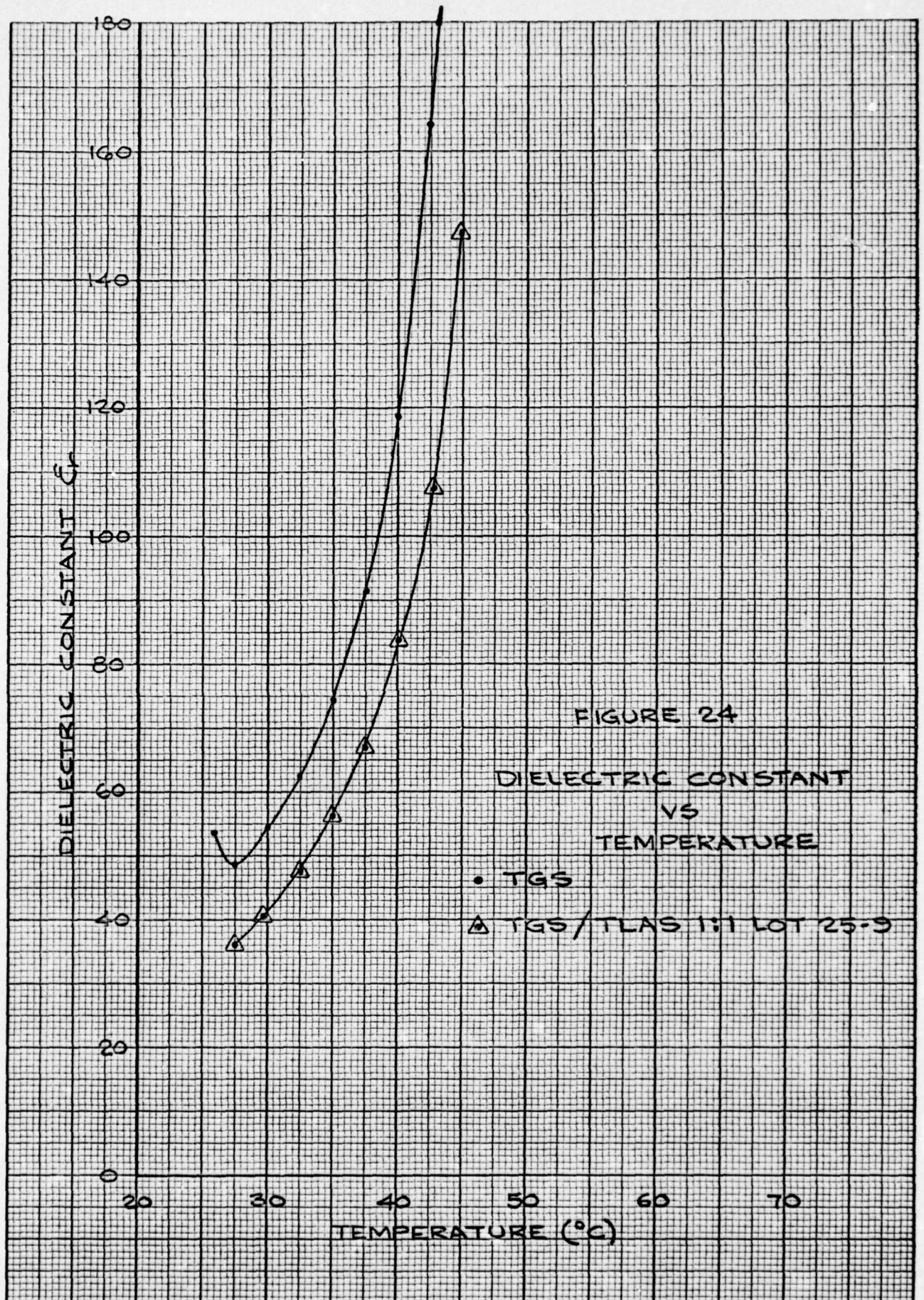
TEMPERATURE ( $^{\circ}\text{C}$ )

| $T^{\circ}\text{C}$ | $\epsilon_r$ |
|---------------------|--------------|
| 27.7                | 36.1         |
| 29.9                | 40.9         |
| 32.5                | 47.8         |
| 35.0                | 56.3         |
| 37.5                | 67.3         |
| 40.0                | 83.9         |
| 42.7                | 107.7        |
| 44.8                | 147.2        |

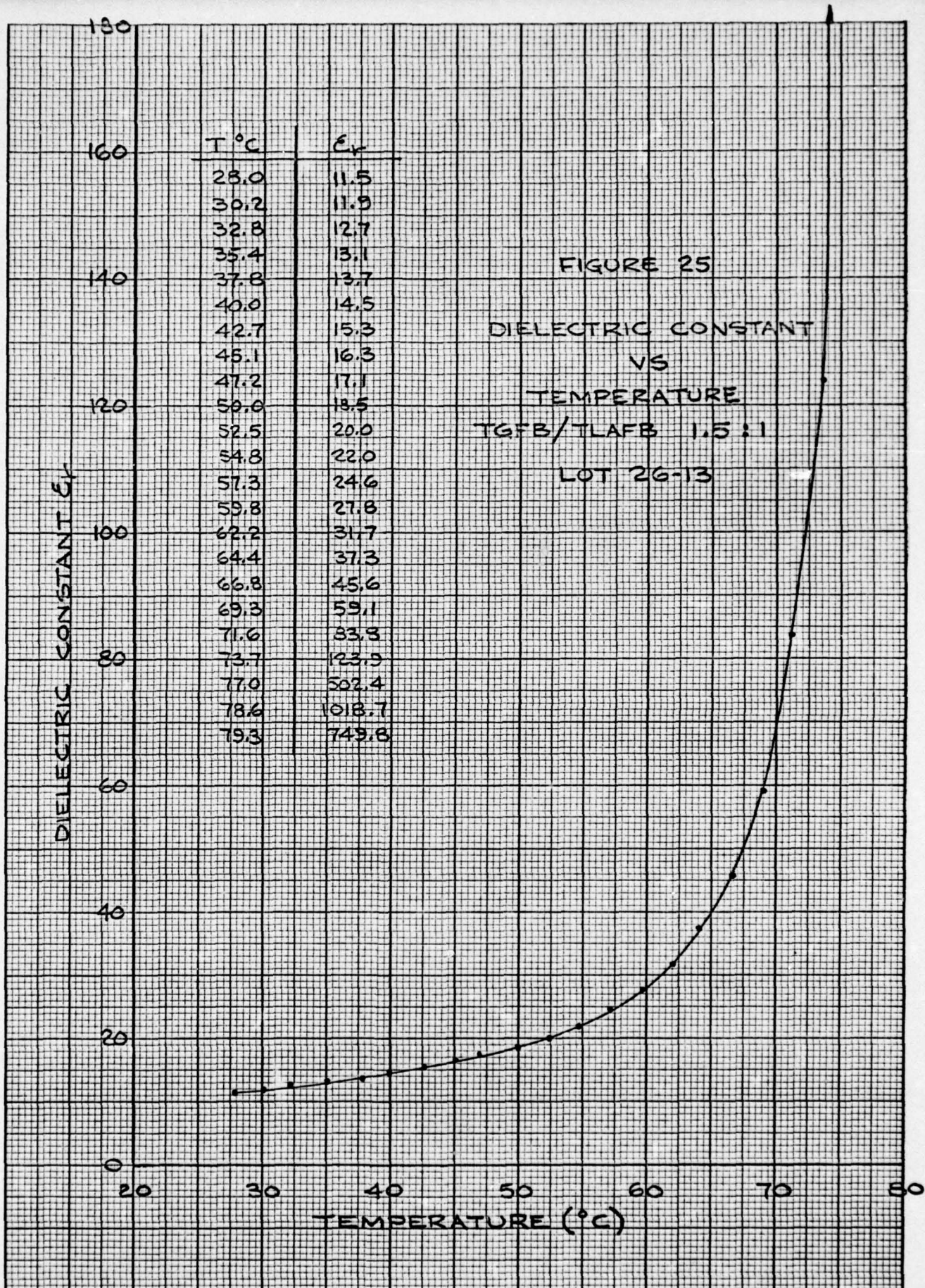
FIGURE 23

DIELECTRIC CONSTANT  
VS  
TEMPERATURE  
TGS/TLAS 1:1  
LOT 25-3

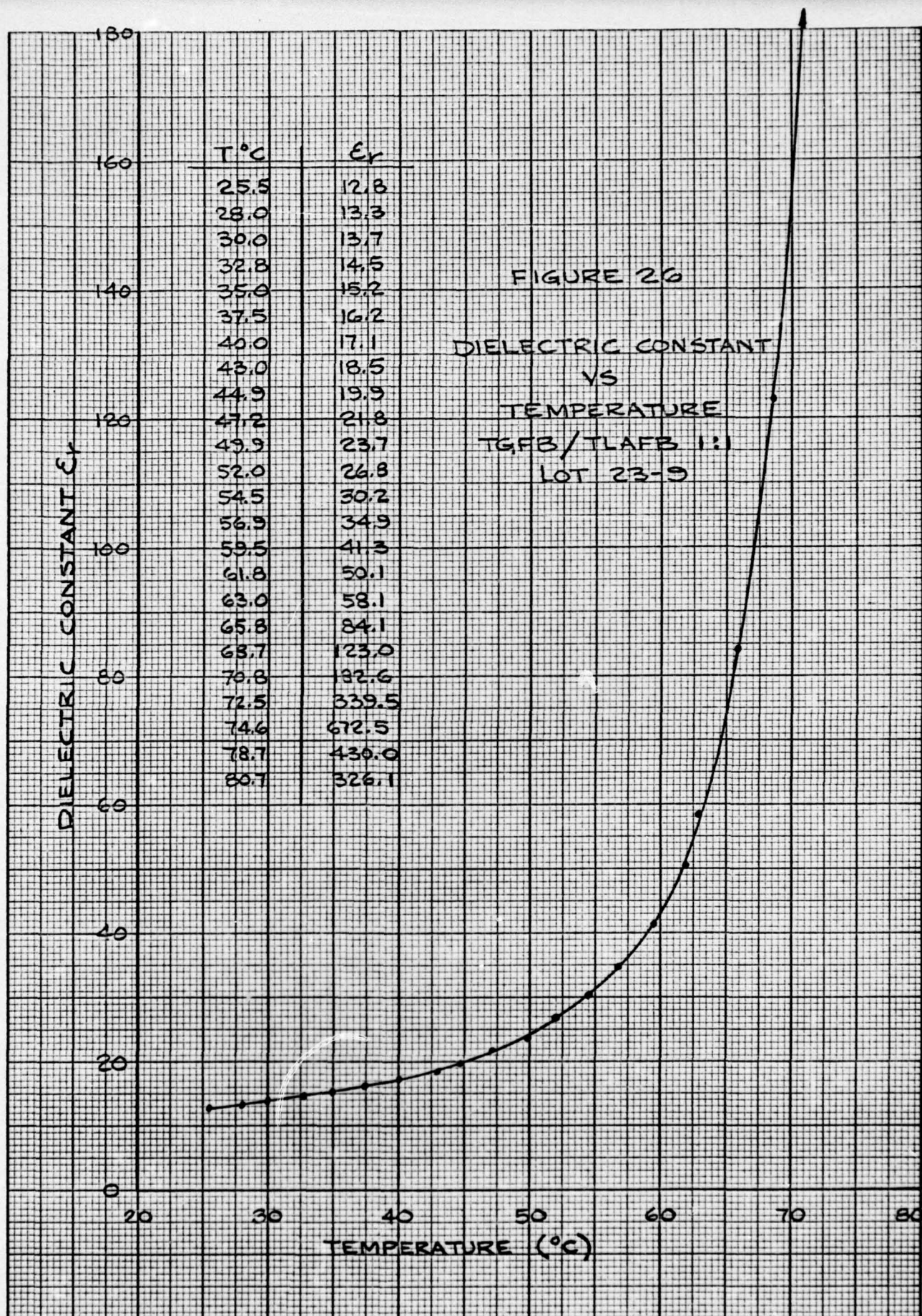




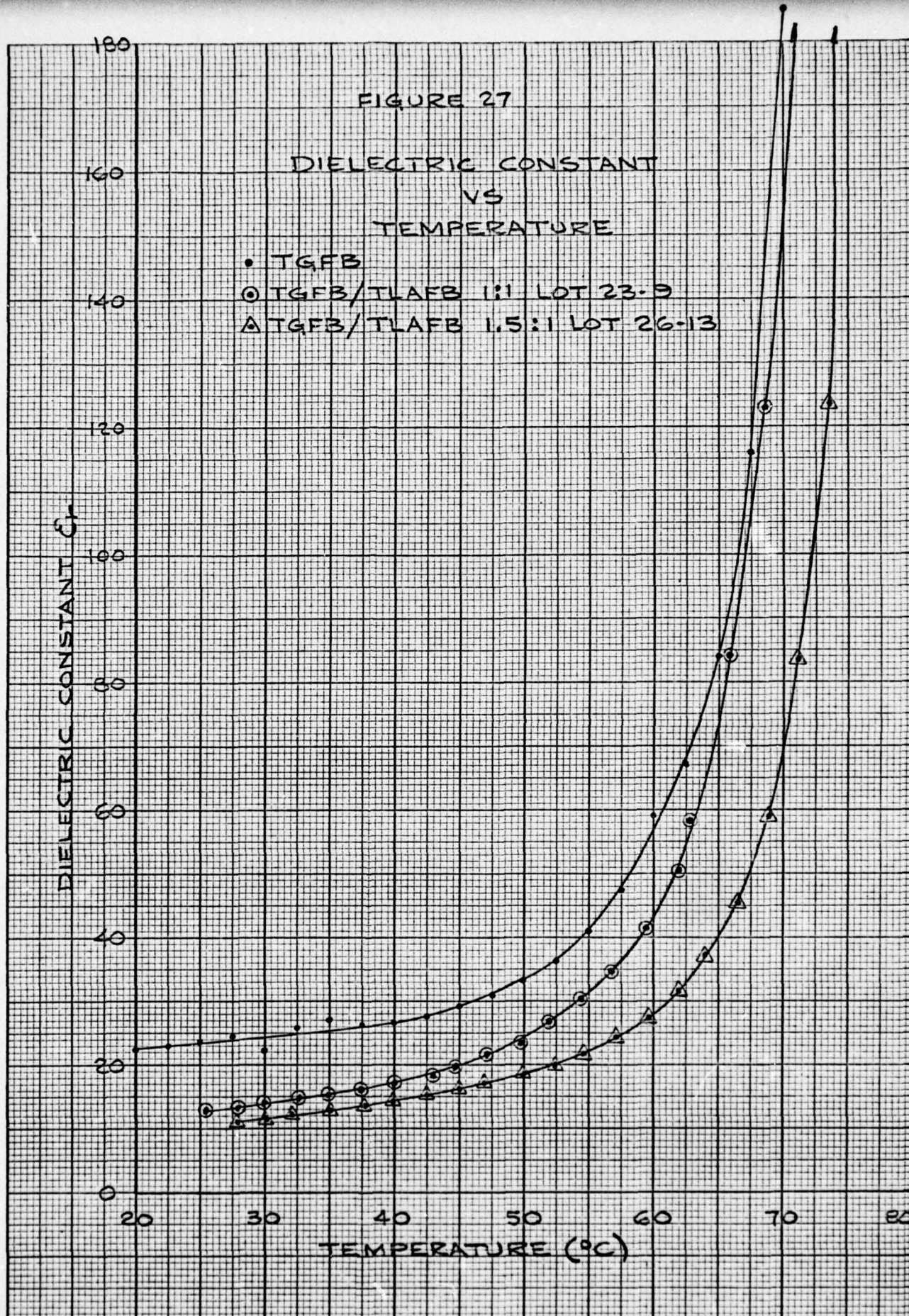












DIELECTRIC CONSTANT  $\epsilon_r$

160

140

120

100

80

60

40

20

20

30

40

50

60

70

TEMPERATURE ( $^{\circ}\text{C}$ )

X =  $19\frac{1}{2}$  V BIAS VOLTAGE APPLIED

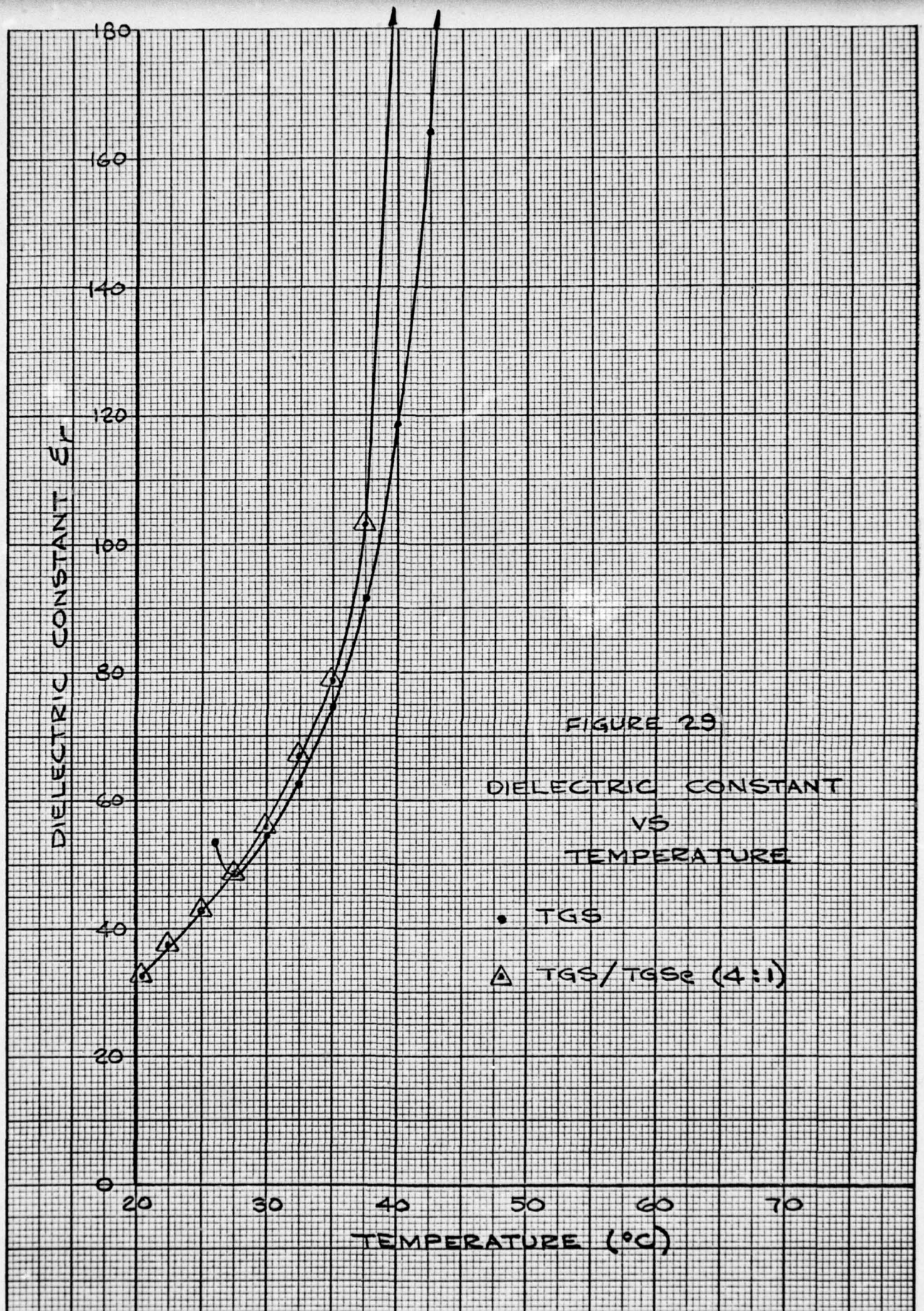
| T $^{\circ}\text{C}$ | $\epsilon_r$ |
|----------------------|--------------|
| 22.5                 | 37.4         |
| 25.0                 | 39.7         |
| 27.5                 | 48.3         |
| 30.0                 | 51.8         |
| 32.5                 | 60.7         |
| 35.0                 | 72.2         |
| 37.5                 | 94.4         |
| 40.0                 | 126          |
| 42.5                 | 189          |

• = NO VOLTAGE APPLIED

| T $^{\circ}\text{C}$ | $\epsilon_r$ |
|----------------------|--------------|
| 20.5                 | 32.8         |
| 22.5                 | 37.4         |
| 25.0                 | 42.6         |
| 27.5                 | 48.3         |
| 30.0                 | 55.3         |
| 32.5                 | 66.8         |
| 35.0                 | 78.3         |
| 37.5                 | 103.0        |
| 40.0                 | 123          |
| 42.5                 | 207          |
| 45.0                 | 382          |
| 47.5                 | 1637         |
| 50.0                 | 2391         |
| 52.5                 | 1033         |
| 55.0                 | 572          |
| 57.5                 | 428          |
| 60                   | 169          |

FIGURE 28  
DIELECTRIC CONSTANT  
VS  
TEMPERATURE  
TGS-TGSe (4:1)





### 5.3 Density

Density determinations were made by weighing known volumes of crystal. Table 7 gives the observed values. The alanine doped crystals did not show significant change in density.

TABLE 7  
DENSITY MEASUREMENTS

| <u>Crystal</u> | <u>Density</u> |
|----------------|----------------|
| TGS            | 1.69           |
| TGFB           | 1.65           |
| D-TGFB         | 1.71           |
| TGSe           | 1.85           |

### 5.4 Figure of Merit

The figure of merit,  $M$ , recommended by NVL is  $M = \frac{P(T)}{c_p \cdot d \cdot \epsilon_r}$  where  $P(T)$  is the pyroelectric coefficient ( $\text{coul/cm}^2 \text{ } ^\circ\text{C}$ )  $c_p$  is the specific heat ( $\text{J/gm}^\circ\text{C}$ ),  $d$  is the density ( $\text{gm/cm}^3$ ) and  $\epsilon_r$  is the dielectric constant. Although some initial work was carried out on specific heat measurements, accurate measurements on the small crystal samples available proved to be too difficult without specialized instrumentation such as a DTA instrument. Time and funds were not available to purchase this equipment and so measurements of specific heat were not made.

Literature values of  $c_p$  for TGS, D-TGS and TGFB do not differ much. We have therefore used literature values<sup>7</sup> of  $c_p$  for TGS and TGFB in all the figures for l-alanine and TGSe coped TGS, literature values of  $c_p$  for TGS were used; for D-TGFB and doped TGFB literature values of TGFB were used. The specific values used were:



| <u>TGS</u>      |                 |        |
|-----------------|-----------------|--------|
| $c_p$ (Cal/Mol) | $c_p$ (J/gm °C) | T (°C) |
| 75              | 0.97            | 25     |
| 77              | 1.00            | 28     |
| 77              | 1.00            | 30     |
| 79              | 1.02            | 35     |
| 83              | 1.07            | 40     |
| 87.5            | 1.13            | 45     |

| <u>TGFB</u>     |              |        |
|-----------------|--------------|--------|
| $c_p$ (Cal/Mol) | Cal(J/gm °C) | T (°C) |
| 75              | 1.01         | 25     |
| 80              | 1.07         | 30     |
| 83              | 1.11         | 35     |
| 85              | 1.14         | 40     |
| 88              | 1.18         | 45     |
| 94              | 1.26         | 50     |
| 109             | 1.46         | 55     |
| 111             | 1.49         | 60     |
| 120             | 1.61         | 65     |
| 135             | 1.81         | 70     |

The figures of merit  $\frac{P(T)}{c_p \cdot d \cdot \epsilon_r}$  for TGS, TGFB, and D-TGFB are shown in Figure 30. The figure of merit for D-TGFB is significantly higher than that of TGS, particularly at temperatures above 45°C. While D-TGFB is better than TGFB at temperatures above 37°, the improvement is not as great as it is compared to TGS.

Figures of merit of alanine doped TGS and TGFB are shown in Figures 31 and 32. It is seen that the addition of

l-alanine does not materially affect the figure of merit with either TGS or TGFB as the host crystal.

Finally, TGS/TGSe shows some improvement over TGS, but both have much lower figures of merit than D-TGFB, as shown in Figure 33.



FIGURE 30

FIGURE OF MERIT  $\left( \frac{P(T)}{C_p \cdot E_n \cdot d} \right)$

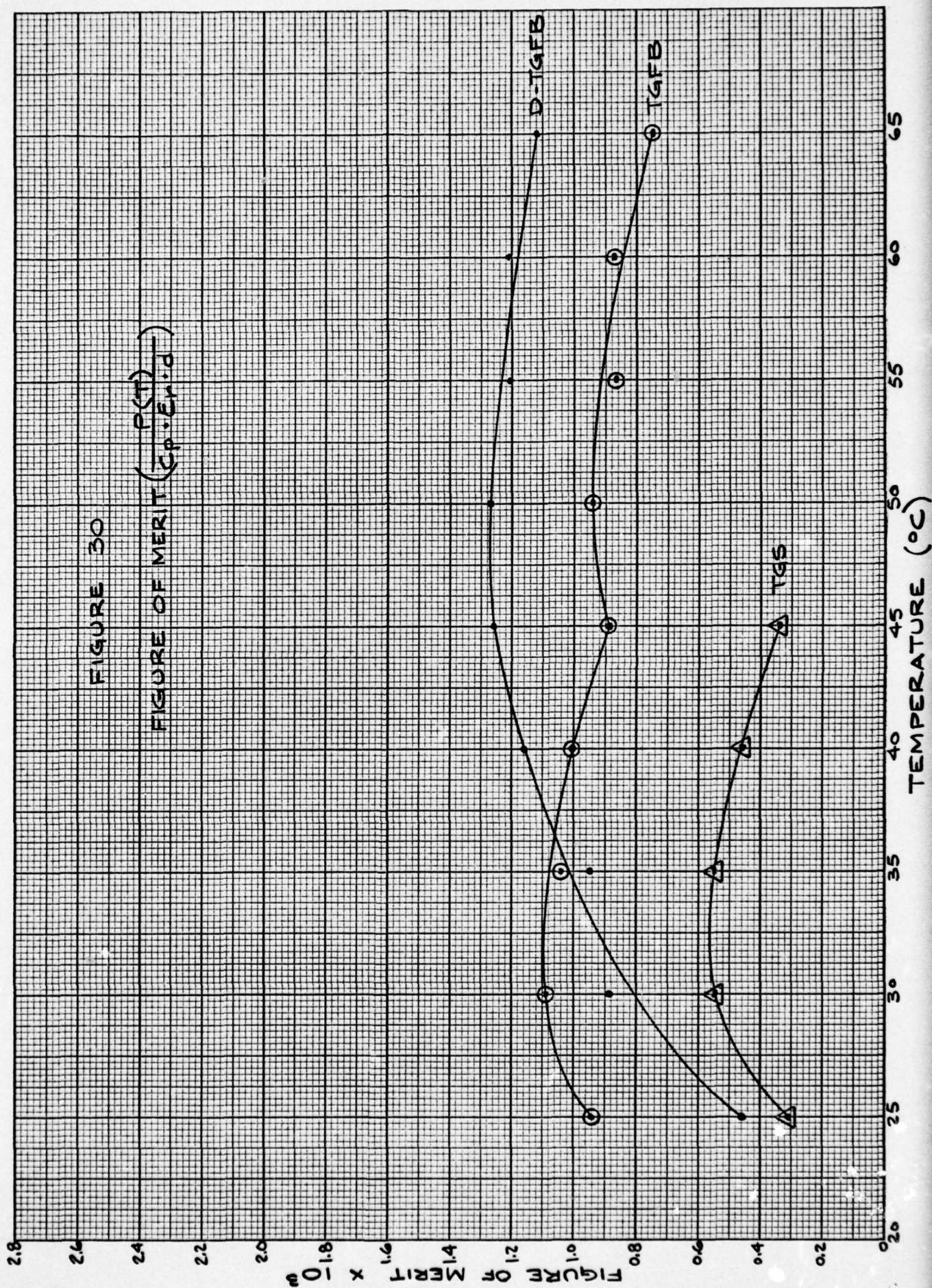
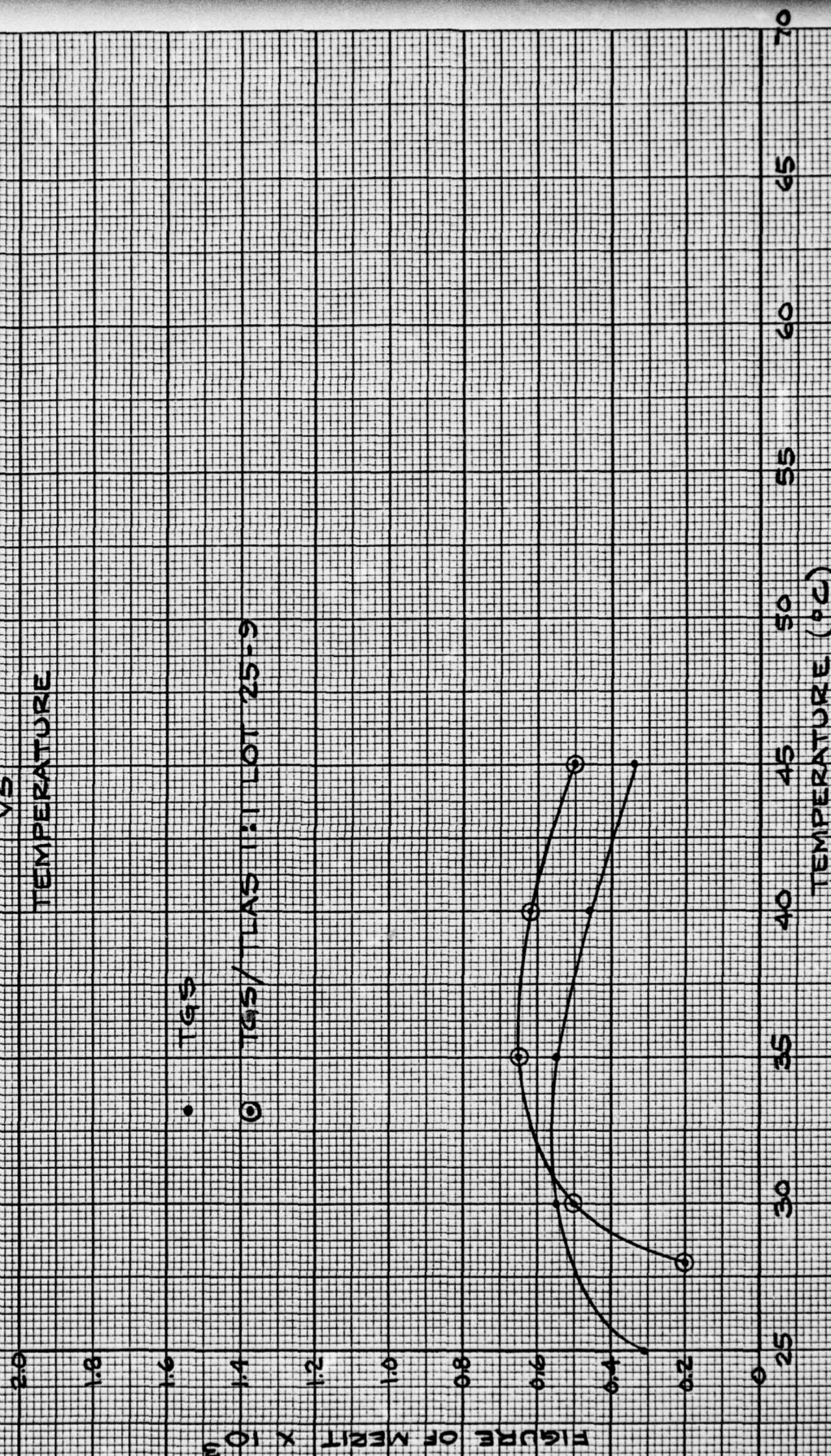




FIGURE 31

FIGURE OF MERIT  $\left( \frac{P(T)}{C_p \cdot \epsilon \cdot d} \right)$   
VS  
TEMPERATURE





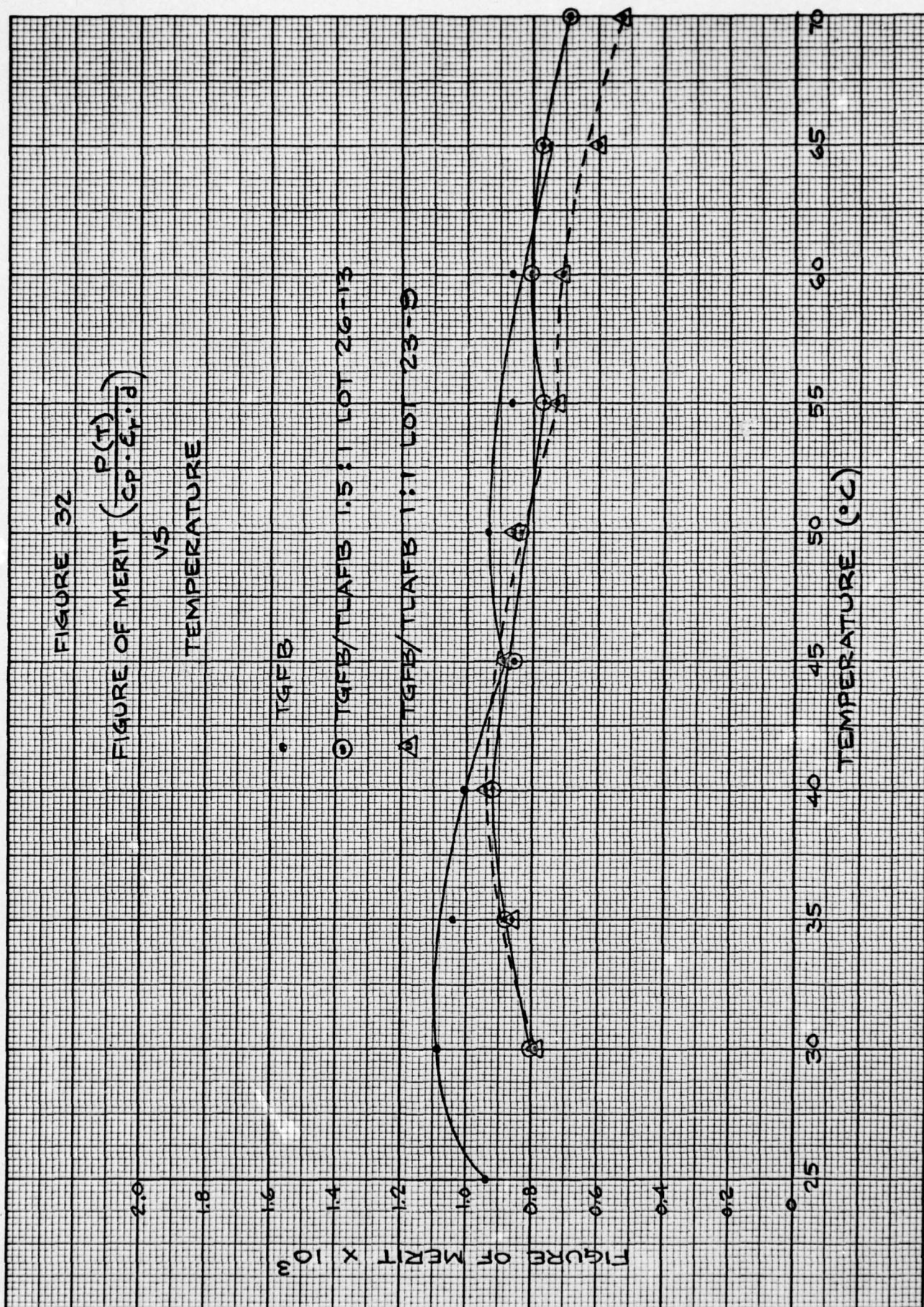
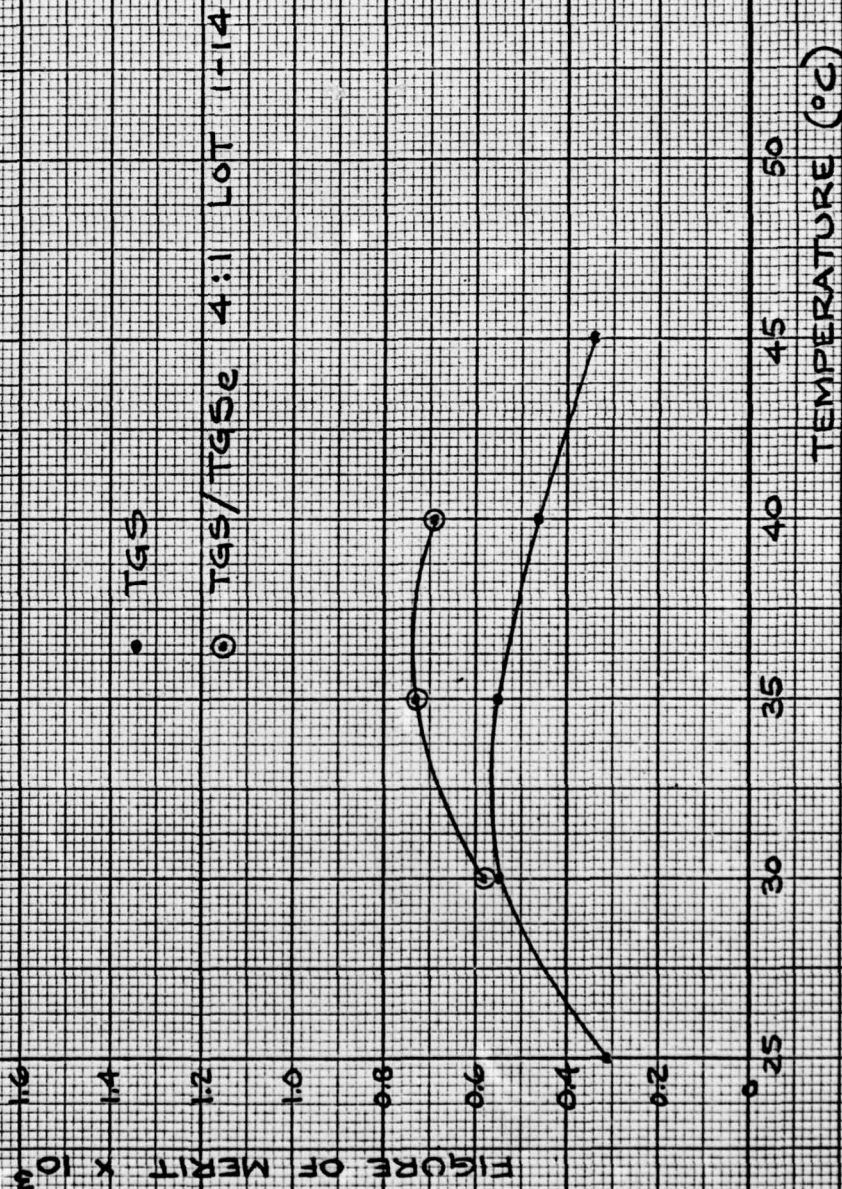




FIGURE 33  
FIGURE OF MERIT  $\left( \frac{P(T)}{C_p \cdot \epsilon_r \cdot d} \right)$   
VS  
TEMPERATURE





## 6.0 PREPARATION OF THIN TARGETS

### 6.1 Optical Polishing Techniques

Vidicon targets of TGS, TGFB, D-TGFB and l-alanine doped TGS were prepared and delivered to NVL. These targets were made according to the following manufacturing process:

1. The crystal boule was cut into an octagonal rod using a string saw.
2. The rod was turned on a lathe to a 18mm dia.
3. The rod was cleaved into plates 2mm thick.
4. Those plates that exhibited clean, flat cleavage faces were selected out and one face of each plate was ground flat.
5. The ground faces of the plates were cemented to a cast iron lap and the opposite faces ground flat and parallel. The upper faces were then polished by hand to approximately  $\lambda/2$ . A final buffing or etching was performed to remove any abrasive that might be left on the crystal surface. This operation was carried out on a soft flannel lap very slightly moist with water.
6. The crystals were removed from the lap, turned over, cemented to a glass optical flat and the second face ground down to thickness and then polished and etched as above.

7. The crystals were removed from the lap cleaned by successive immersion in xylene, and dried.

8. The thickness of the target was measured by an Olympic electronic gauge accurate to 0.25  $\mu$ .

In this way it is possible to prepare targets as thin as 20 - 25 microns. Below this thickness the targets were very fragile and the attrition rate in manufacture was very high.

## 6.2 Cup-Etching

### 6.2.1 Introduction

It has been found that D-TGFB pyroelectric targets for vidicons give improved results if the target thickness is in the order of 15 microns. It is very difficult to manufacture targets this thin by the optical polishing technique outlined above. Handling such thin targets during shipment and processing also presents considerable problems.

Targets made by cup-etching can be made as thin as 15  $\mu$ , and the thick rim adds the strength needed for subsequent handling.

Subsequent sections describe the various experiments that were carried out in an effort to develop an etch etching process suitable for D-TGFB. All the initial experiments were carried out with TGS because it was readily available and much lower in cost.



### 6.2.2 Etchants

Cleaved and ground TGS blanks 20mm in diameter and 2mm thick were used. A crystal was mounted on a flat plate attached to the bottom of a rod which was driven by a motor. The crystal and holder were placed in a beaker containing the etchant so that the crystal faced downward. The crystal was rotated at 15 rpm.

TABLE 8

| <u>Experiment<br/>Number</u> | <u>Etch<br/>Time,<br/>min.</u> | <u>Etchant</u>   | <u>Results</u>  |
|------------------------------|--------------------------------|--|---|
| 1                            | 6                              | pure glycol  | no etch   |
| 2                            | 6                              | pure isopropanol   | no etch   |
| 3                            | 6                              | 20 ml isopropanol<br>25 ml water                                       | no etch   |
| 4                            | 6                              | 20 ml isopropanol<br>15 ml water                                       | no etch   |
| 5                            | 5                              | 10 ml isopropanol<br>40 ml water                                       | very deep etch, bubbles on crystal surface                                |
| 6                            | 9                              | 15 ml isopropanol<br>30 ml water                                       | excessive etch  |
| 7                            | 5                              | 20 ml isopropanol<br>25 ml water                                       | no etch   |
| 8                            | 6                              | 20 ml isopropanol<br>30 ml water                                       | good etch on cleaved surface  |
| 9                            | 3                              | 20 ml isopropanol<br>30 ml water<br>(rim on edge protected by varnish) | good polished surface, some orange peel effect, depth of etch 15-20 $\mu$ |

The 2:3 isopropanol:water etchant looked promising and work was continued with this etchant.

### 6.2.3 Ultrasonic Agitation

TGS plates were placed in an ultrasonically agitated tank to determine if the stirring would produce a more uniform surface. Severe pitting and poor surfaces were obtained. This approach was abandoned.

### 6.2.4 Auxiliary Stirring

In addition to rotating the crystal, a stirrer was inserted in the etchant solution to try to improve the flatness of the surface. The etched surface was still very high in the center and low at the rim.

The crystal was then attached to the shaft so that it was displaced from the shaft and rotated in the solution with the flat face perpendicular to the direction of rotation. Although it was felt that this would expose the crystal surface more uniformly to the etchant, the etched surface was still high in the center and low at the base of the rim. When a crystal without a rim was used, the etched surface was very smooth but was convex, falling off sharply at the edges.

Another series of experiments were then performed in which the motor and stirring shaft were placed at about 45° to the vertical to determine whether agitation and etching would be more uniform. No improvement was observed.

### 6.2.5 Saturated TGS Solution

An aqueous solution of TGS was prepared that was saturated at 21°. It was then heated to 24° to lower the saturation and then used as an etchant. The TGS surface finish was poor. When the crystal was dipped in pure isopropanol to quench the etching, small crystals of TGS precipitated out on the surface. This approach was abandoned.



#### 6.2.6 Effect of Rotation Rate

TGS plates with finely ground surfaces and a 1.5mm wide rim protected by painted on varnish were used. The plates were rotated in a 2:3 isopropanol - water etchant at various rotation rates. Rates above 15 rpm resulted in even higher center regions than in the plates made by rotation at 15 rpm. That is, the center region was thicker than the thickness at the edge of the varnish layer.

#### 6.2.7 Effect of the Protective Rim

Even though the rim on the crystal blanks as formed by a painted layer of varnish was only a few mils thick, an experiment was carried out to determine if it had any effect on the undercutting problem. A rim was prepared by evaporating gold on the crystal blank. When etched in 3:2 isopropanol-water a very flat etched surface was obtained with no undercutting. However, the gold rim was porous. A very thin varnish layer sprayed on with a spray gun produced a satisfactory rim that gave flat etched surfaces.

#### 6.2.8 Planetary Rotation Device

In an effort to obtain uniform stirring of the etchant solution, the apparatus shown in Figure 34 was built. The crystal blank, after spraying to produce a thin rim (approx. 1.5mm wide), was mounted on a pedestal which was screwed into the top of the crystal rotation wheel assembly. The assembly was lowered into the solution jar and the motor started. With 1:1 isopropanol-water etchant at 23°C and a polished TGS crystal plate 135 microns thick, a target was prepared as shown in Figure 35. It required 100 minutes to etch off 120 microns. The thickness of the target was measured with the Olympic electronic gauge by placing the target on a smooth, flat gauge block.

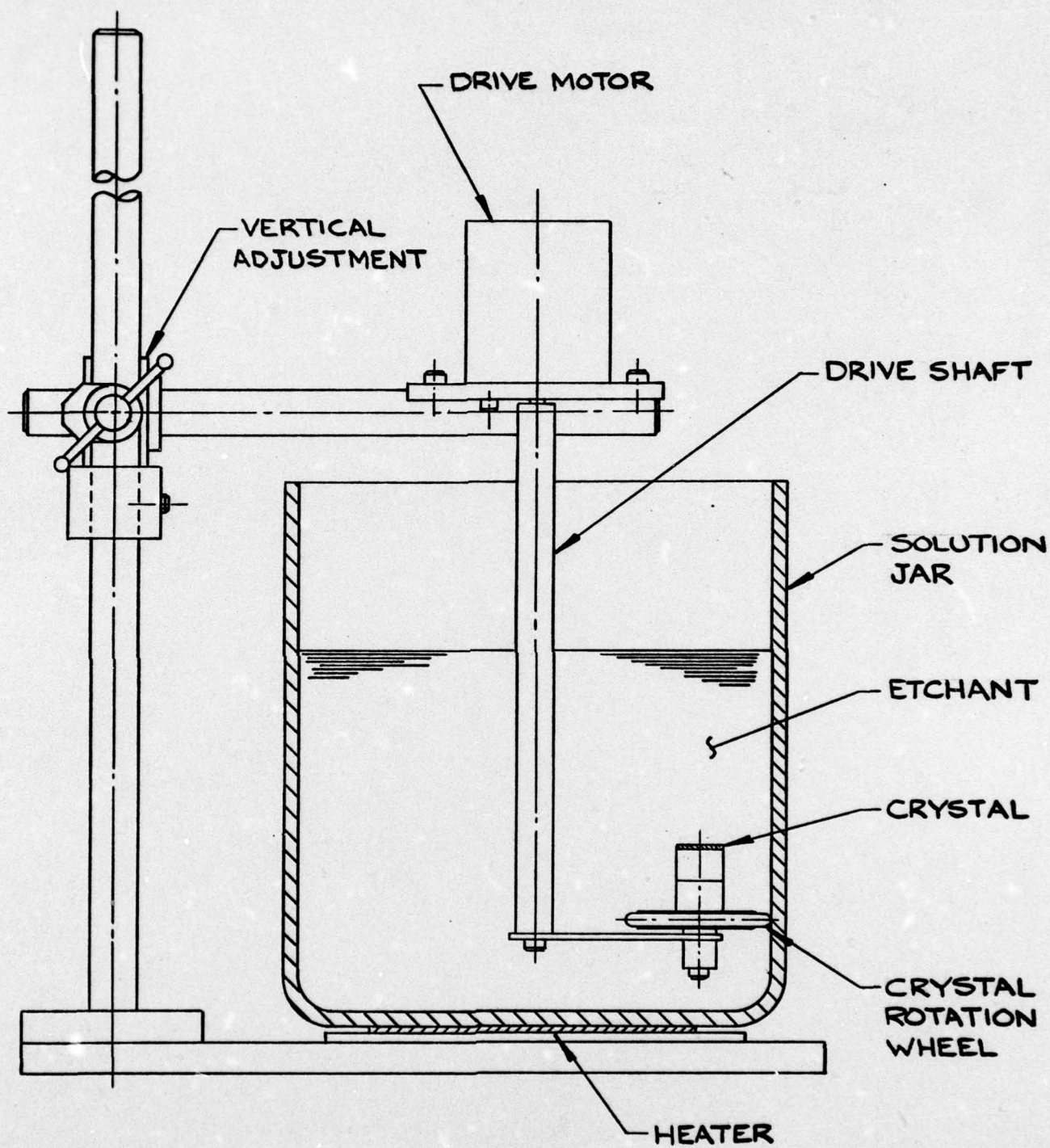


FIGURE 34  
PLANETARY ROTATION ETCHING APPARATUS



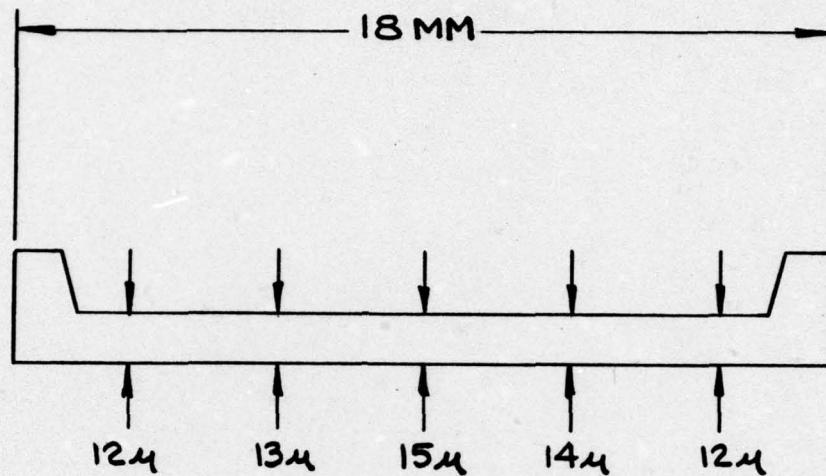


FIGURE 35

CUP-ETCHED TGS TARGET SHOWING  
FINAL THICKNESS OF TARGET AT  
VARIOUS PLACES. STARTING  
THICKNESS OF BLANK WAS 135μ

#### 6.2.9 Cleanliness of Etchant Solution

Some blemishes were observed in the cup-etched TGS targets. To determine if this was caused by particulate matter in the etchant solution, several experiments were carried out with etchant solution filtered through a 0.6  $\mu$  millipore filter. No improvement was observed. It was concluded that the blemishes come from the target or particulate matter introduced during etching.

#### 6.2.10 D-TGFB Targets

The initial experiments with D-TGFB crystal blanks and 1:1 isopropanol-water etchant failed because the blanks dissolved completely. The ratio of isopropanol to water was increased in successive runs to 4:1 isopropanol-water. At this concentration the etch rate was 1.5  $\mu$  per minute at 23°C. The surface finish was poor, and fogged as soon as the crystal was cleaned with xylene.

Experiments with ethylene glycol and ethylene glycol-water mixtures did not yield materially better surfaces.

The etching apparatus is considered satisfactory, but different etchants are needed to overcome the very high solubility of D-TGFB and its sensitivity. Inadequate time and funds were available to continue the etchant studies.



## 7.0 DISCUSSION OF RESULTS

### 7.1 Crystal Growth

Growth conditions were established for growing TGFB and D-TGFB single crystals of good quality in sizes up to approximately 5 cm x 5 cm x 5cm. The crystals were grown in lucite or polycarbonate tanks with seed holders, shaft, and cover plates of lucite. In the case of D-TGFB the deuteration level of the labile hydrogen positions was 92 percent. The crystal quality was good as evidenced by clean, flat cleavage, freedom from twins, and the absence of veils, cracks or inclusions.

The optimum crystal growth conditions for TGFB and D-TGFB were:

1. Starting saturation temperature of 45°
2. Seed rotation rate of 15 rpm.
3. pH of 3.6.
4. Growth rate of 0.1° per day for a 10 liter nutrient solution.
5. A seed orientation with the cleavage parallel to the horizontal.
6. Seed holder consisting of a rotating horizontal plate on which the seeds were cemented.

TGS and TGFB crystals doped with l-alanine were grown, but with considerable difficulty. Best results were obtained by starting with low l-alanine concentrations in the nutrient solution and pure TGS or TGFB seeds. The best crystals from the first runs were used as seeds for the next runs in which the l-alanine content was higher. This procedure was continued until the l-alanine content was too high for clear growth.

Although some good crystals of l-alanine doped TGS and TGFB were grown and fabricated, it was found that the crystals were considerably more fragile and susceptible to cracking than the pure undoped crystals. The attrition from crystal boule to polished electroded sample was very high.

TGS-TGSe crystals were grown, but they unexpectedly acted like selenium doped crystals rather than as solid solutions of TGS and TGSe. It was very difficult to introduce selenium into the TGS lattice and even the best quality crystals were quite fragile and highly susceptible to cracking.

## 7.2 Crystal Properties

Measurements of pyroelectric coefficient and relative permittivity of TGS, TGFB, D-TGFB, l-alanine doped TGS and TGFB and TGS-TGSe crystals led to the following conclusions:

1. The figure of merit,  $\frac{P(T)}{c_p \cdot d \cdot \epsilon_r}$ , was highest for D-TGFB. Even though D-TGFB has a lower pyroelectric coefficient than TGS, it has a much lower  $\epsilon_r$  than TGS.
2. l-alanine doping of TGS or TGFB did not improve the figure of merit.
3. The l-alanine doped crystals were more fragile and prone to cracking than the undoped crystals.
4. The properties of TGS:TGSe crystals were very similar to l-alanine doped crystals and did not act as solid solutions. No advantages of TGSe doping were found.



### 7.3 Thin Targets

Targets of TGFB and D-TGFB 18mm in diameter and as thin as 20 to 25 microns were successfully made by optical polishing techniques.

Considerable difficulty was encountered in preparing cup-etched targets. All the initial experiments were performed with TGS crystals because of its greater availability. At first uniformity of thickness was a major problem. With adequate masking and with stirring designed to present etchant uniformly to the crystal surface, uniformly etched targets were obtained using isopropyl alcohol-water as the etchant.

When the same technique was applied to D-TGFB, the greater solubility of D-TGFB compared with TGS made control of the etching rate much more difficult. The rapid attack of the etchant on the D-TGFB produced a poor surface. Attempts to slow down the etching rate by increasing the non-aqueous components of the solvent helped but did not solve the problem. Freshly etched surface of D-TGFB were found to be very sensitive to fogging and had to be protected from even low humidity atmospheric air. There were inadequate funds and time to continue this phase of the program.

Further work on cup-etching of D-TGFB should include investigation of other polar type etchants such as DMSO(dimethyl sulfoxide), glycerol, dioxane, and methyl alcohol, with and without the addition of water.

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